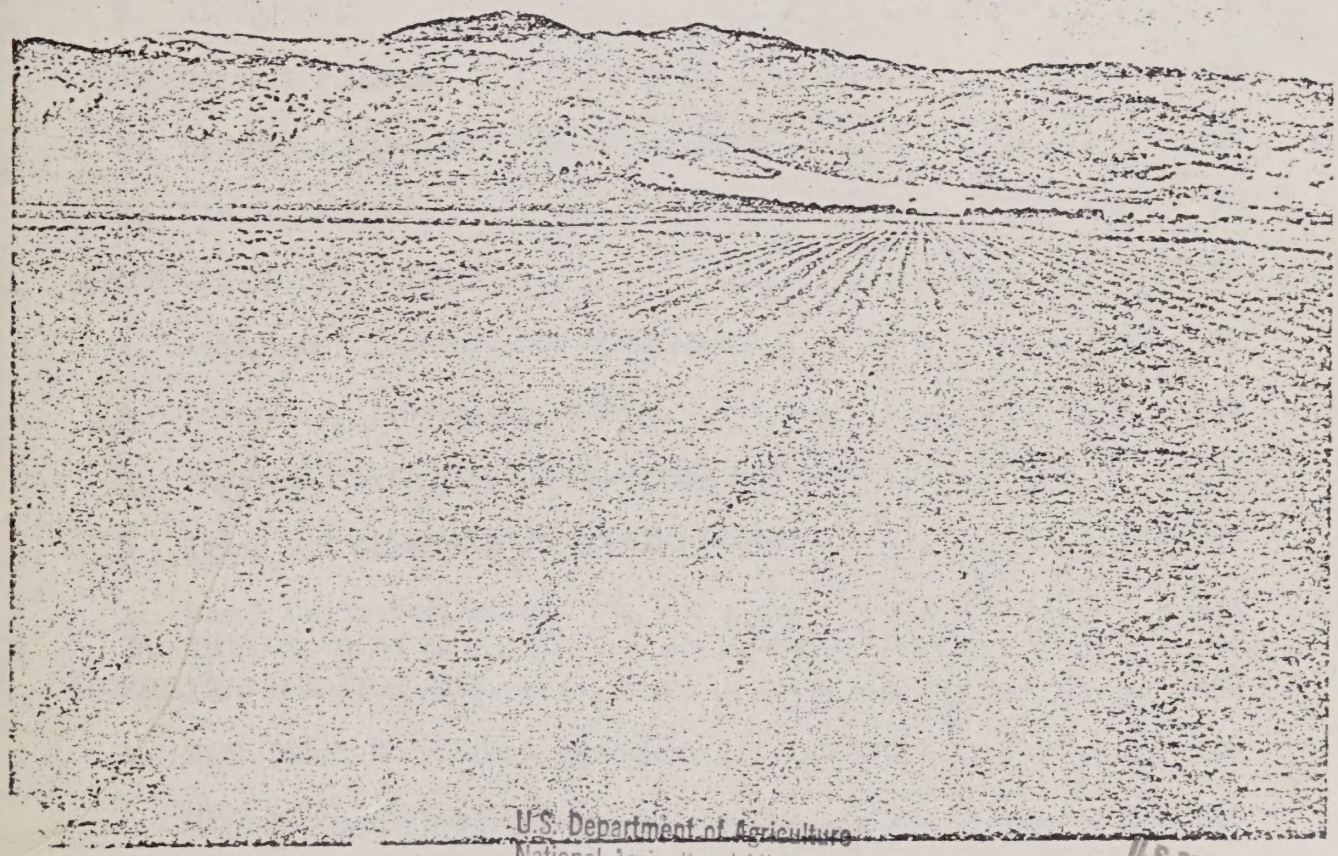
Final Report

NATURAL RUBBER EXTRACTION AND PROCESSING INVESTIGATIONS

U S NATURAL RUBBER RESEARCH STATION

Salinas, Calif. April 30, 1953



BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
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FINAL REPORT

Natural Rubber Extraction and Processing Investigations Project

INDEX

In general, there were two distinctly different operational phases necessary in the program of the Natural Rubber Extraction and Processing Investigations Project in process research and development. The first of these was the reconstruction of the pilot plant. The second was the carrying out of experiments to determine the effect of different processing steps upon the recovery of rubber and its quality, and the development of specialized equipment needed for the various operations.

2. Objectives

Two overall objective statements have guided the work of the Natural Rubber Extraction and Processing Investigations Project during the past five years. The first governed the work from August 1947 to June 30, 1949, at which time the fund reduction necessitated the curtailment of objectives. The first statement of objectives called for the development, through laboratory and pilot plant investigations, of new or improved methods for the extraction and processing of natural rubber from domestic rubber-bearing plants; the utilization of byproducts from such plants; investigation of analytical methods; and fundamental studies of rubber and non-rubber components.

The second set of objectives, which covered the period July 1, 1949 to the Project's close, were directed to the development, through laboratory and pilot plant investigations, of new or improved methods for the recovery of crude rubber of uniform high quality from guayule shrub; to characterize the resins and other components of crude rubber which affect quality; and to develop means of stabilizing the quality of the rubber.

3. Reconstruction of the Pilot Plant

Both of the above objective statements indicated emphasis on rubber quality. A review of all previous work, including both that of private enterprise and of the Emergency Rubber Project, indicated that quality of rubber was influenced by the character of the raw material entering the mill circuit. The last point at which the shrub (and therefore the rubber) possess the greatest uniformity is when it is a stand of living plants in the field which have been accorded reasonably uniform culture throughout their lives up to the day before they are dug. It is at this point, too, that the rubber has all the inherent qualities as produced by the plant. As soon as the plants are harvested, the rubber in them is subject to modification by many external factors. To study the changes that occur after harvest, to measure the effect of various treatments on the shrub, to evaluate differences in rubber yield studies as influenced by various treatments---all of these required the measurement of differences so small that the work would have to be planned and carried out in such a fashion that statistical evaluation of the results would be possible. The pilot plant, as it was in 1947, was totally unsuited for research of this type. That made necessary the removal of existing equipment and the procurement and installation of suitable facilities

a. Removal of Old Equipment. The equipment removed consisted of three large batch pebble mills, six wooden tanks of approximately 3000 gallons each, a combination tunnel and flash drier, a large attrition mill, a cane mill, and

many miscellaneous small items. Many of the items were removed by available staff personnel during the recruitment period. The heavier items were removed by contract.

b. Installation of New Equipment. Reconstruction work in the pilot plant did not occur all at once. The first thing that was required was a series of small batch mills with which to carry out closely controlled experiments on storage of shrub, shrub pretreatment studies, and investigations centering about rubber hydrocarbon recovery. The equipment required to carry out this work included a battery of four 27-inch batch pebble mills, two pailas, one scrub mill, a centrifuge for separating the flotation liquor into its two components (bagasse and effluent), and an effluent tank. Concrete flotation tanks were required for each of the batch and scrub mills, and each of the pailas. A triplex hydraulic pump and accumulator tanks supplied hydraulic pressure of 500 p.s.i.g. for the pailas. Various pumps and piping were needed for moving the slurries, flotation liquors and the like, as necessary. A hammermill and crushing rolls in the shrub preparation department made possible variation in shrub pretreatment. All this installation work, including the electrical wiring, was done by personnel of the Process Research and Development Section.

On July 2, 1948, all personnel had been recruited, the above phases of pilot plant reconstruction were complete, and process research got under way.

Later on, as time permitted and as the research program required, there were installed other items of equipment. This equipment and attendant facilities made possible investigations of a continuous process circuit. They included tube pebble mills and jordans for continuous milling; a rectangular flotation tank fitted with bagasse removal facilities and a continuous centrifugal filter for continuous flotation studies; and a high pressure, automatic decorking device, called a "baica" for continuous decorking. This last unit had been developed and constructed during the Emergency Rubber Project, but had not been tested in a continuous production circuit.

4. Lines of Research Investigated

a. Development of Control Milling. Considerable work had been done in the past on what were called "control" millings in research on the production of worm rubber from guayule. Critical examination of this work indicated almost consistent failure to maintain total rubber and solids balances throughout any given experiment, and there was rarely any determination of the reproducibility of any method. Hardly ever were controls run in exactly the same way on raw materials that had been handled exactly alike. Frequently, inadequate or improper sampling confused the interpretation of the experimental data.

The vagaries of the weather during the period of field cure and the biologic nature of guayule were often overlooked. Consequently, unknown factors influenced the data and could not be taken into account in interpreting the information obtained. These inadequacies led to the conclusion that the objectives of current process research could best be met by the application of experimental designs and statistical treatments of the resultant data as commonly used by biological scientists. A series of experiments was planned and carried out to develop a control system of milling in which the degree of

reproducibility would be known, and in which the factors which caused uncontrolled variation could be segregated and their effects measured.

An evaluation of the experimental data resulted in the formulation of a control milling procedure as here described.

A block of plants in the field from which the material is to be used for the experiment is selected in which the plants appear to be uniform as to plant size, vigor, and growth characteristics. This block is rogued to remove all plants that are off-type when the experiment to be run involves the testing of different types of machines or different operative procedures. When the experiment is of such nature that it takes field variability into consideration, the plants are selected by random number. In either case, the plants required are harvested and delivered to the pilot plant as soon as possible after digging.

The plants are then parboiled for 15 minutes at a temperature of 200° to 205° F. and then passed through the trommel for defoliation. When defoliated, they are cut in a fly-knife cutter through a 1/2-inch screen.

Samples are taken from the cut shrub for analytical determinations of rubber, resin, and moisture. The remaining shrub is crushed twice at a roll clearance of approximately 0.002-inch, then hammermilled once through a 1/2-inch screen using straight hammers. After hammermilling, the material is divided into the required number of replicates. Each replicate is immediately sampled for an analytical moisture determination, and a rapid moisture determination on a Dietert moisture teller.

As soon as the results from the rapid moisture determination are available, the mill charges are weighed out on a dry weight basis according to the volume of the mill in which each replicate is to be processed. Each mill charge is labeled and placed in a covered can. All control charges are held overnight before milling.

The replicates are milled in 27-inch batch pebble mills. Milling is accomplished at a water-to-solids ratio of 4.5 to 1 and a pebble-to-solids ratio of 20 to 1. Mills are run at 80% of their critical speeds and the initial mill temperature is 85° F. Milling is carried out for 60 minutes. Between 10 and 15 minutes after milling is started the mill is stopped, the lid is removed, and the shrub that becomes packed between mill and lid is carefully replaced in the mill. The lid is then replaced and milling continued. A record of the time for lid removal and replacement is kept so that the exact milling time of 60 minutes is maintained.

At the end of the milling period the mill is filled approximately half full of water and the contents, except for the pebbles, discharged into the flotation tank. The mill is rinsed with copious amounts of water 5 times. On the fourth rinse the mill lid is replaced and the mill is run for 5 revolutions before it is emptied. When rinsing is complete, hot or cold make-up water is added to the flotation tank until a water-to-solids ratio of 100 to 1 at a temperature of 100° F. is reached.

When the correct flotation ratio and temperature are attained, the floating rubber is skimmed off. When the initial skimming is completed, the flotation

liquor is agitated with an electric mixer for 5 minutes, allowed to settle for 5 minutes, and then skimmed again. This agitation and settling process is repeated once, followed by a third skimming. The crude rubber and cork recovered by skimming are held in appropriate sample cans in clean warm water. If it is necessary to hold the rubber for any length of time before decorking is done, a hold-down cover is placed on the rubber to keep it submerged.

Decorking is done in a paila preheated to 200° F. before the rubber is placed in it. The rubber, with about three times its volume of water, is introduced into the paila and brought to a rolling boil. Immediately after boiling, the rubber in the paila is placed under hydraulic pressure of 500 pounds per square inch for 90 minutes. This treatment collapses the cells of the cork granules and renders them susceptible to waterlogging.

After the decorking treatment, the rubber is discharged into a flotation tank at an approximate water-to-solids ratio of 400 to 1 and a minimum temperature of 140° F. The rubber is skimmed from the flotation tank and held in warm water for scrub milling.

The 27-inch scrub mill is preheated to a minimum temperature of 140° F. The rubber charge is then placed in the mill with a pebbles-to-solids ratio of approximately 20 to 1. Water is added and steam is introduced to the scrub mill until the charge is brought up to a minimum temperature of 140° F. and a water-to-solids ratio of at least 20 to 1. Scrub milling is done for 15 minutes. Then the mill is emptied and rinsed thoroughly. The rubber is floated at an approximate water-to-solids ratio of 400 to 1 and at a minimum temperature of 140° F., after which the rubber is skimmed onto drying trays and spread to a uniform depth.

The addition of preservative or antioxidant to the rubber at this point is governed by the nature of the experiment. The rubber is dried in a through-circulation drier with gradually increasing temperatures as follows: Initial temperature of 100° F. for 7½ minutes; 125° F. for 7½ minutes; 150° F. for 7½ minutes; 175° F. for 7½ minutes; and 200° F. for 30 minutes. The trays of rubber are then weighed, replaced in the drier at 200° F. for 5 minutes, then weighed again. This is repeated until a constant weight is reached. When dry, samples for chemical analysis are taken, and the total weight of the crude rubber is obtained.

To determine rubber losses in process, the liquor from the primary flotation tank is passed through a perforated basket-type centrifuge. The flotation tank and the pipe lines are thoroughly washed out. The centrifuge is allowed to run for 5 minutes after the final wash water has passed through in order to reduce the bagasse to an approximately uniform moisture content. The wet weight of the bagasse is obtained and three 1-quart representative samples of bagasse are taken for the analytical determination of rubber, resin, and moisture.

The effluent from the centrifugation is stored in a tank and the volume determined, after which it is agitated violently with an electric mixer and, while the agitation continues, three 1-quart samples are removed for analysis for rubber, resin, and total solids.

All flotation temperatures and ratios are held within the stated limits in the interest of uniformity in procedure, but are not necessarily optimum or applicable to factory operation.

During the course of the experiments, a sample dividing mechanism was devised and fabricated. The divider consisted of eight compartments or boxes with a common base so arranged that they could be rotated mechanically at a constant speed. The outer end of each compartment constituted a removable door through which the shrub samples would be removed after division. The prepared shrub was fed into the eight rotating compartments by utilizing an inclined screw conveyor fitted with a feed hopper and a suitable electrical drive. Use of this machine gave more uniform results than could be obtained with a Jones binary sample splitter and eliminated much manual labor.

The use of a fly-knife cutter in the control milling procedure was necessary for two reasons. First, the hammermill available for pilot plant operations had a feed throat so constricted that whole shrub could not be passed through it. Second, it had been established that chemical analysis of material that had been crushed and hammermilled had a greater degree of variation and lower reproducibility 3/, than material which had been cut only.

Utilization of the control milling procedure described above resulted in a high degree of accuracy and reproducibility. A total solids balance can be maintained with a very reasonable experimental error. In a test designed specifically to test accuracy and reproducibility, a total solids balance of 100.7 percent, with a standard deviation of 2.7 percent, was obtained. Rubber hydrocarbon gave a balance of 101.6 percent with a standard deviation of 1.3 percent. Total resin accountability was low, but consistently so. It gave a balance of 88.3 percent with a standard deviation of 1.8 percent.

b. Storage Studies. With the development of a satisfactory control milling procedure, attention was directed to the possibility of storing the shrub prior to milling. Uppermost in mind during this work was the premise, earlier stated, that the shrub and its constituents possess the greatest uniformity as a stand of living plants in the field. Nevertheless, it seemed that some form of surge storage would be desirable in commercial mill operations to provide a reserve supply of shrub for milling in the event inclement weather or other factors caused a suspension in harvest activities. In addition, it was desirable to compare yields and quality of rubber obtained from freshly harvested shrub with that from shrub that had been stored.

A complete review of all previous storage studies was made. Unfortunately, all of them were open to question one way or another. One of the most important points was whether at the end of the storage period, or at intermediate periods of storage, there was actually as much rubber in the shrub as there was when it was a living plant in the field. A series of experiments was designed which incorporated the two methods of shrub storage most highly recommended for commercial operations, and also shrub which was processed fresh from the field.

3/ Later work on analytical methods resulted in a series of operations which afforded greater accuracy than the methods used when these experiments were carried out.

All three types of shrub were handled by the same operational steps for the recovery of the crude rubber. The two methods of storage were (1) shrub dug and field cured for 7 days, baled with leaves on and stored up to 6 weeks, then parboiled, defoliated and milled; and (2) shrub dug and hauled to pilot plant at once, parboiled and defoliated, stored up to 6 weeks and milled. The control consisted of shrub harvested and processed with a minimum of delay.

(1) Baled - leaves on. Under the conditions of this experiment, increased periods of storage with the leaves on caused a decreased yield of rubber hydrocarbon in the crude. There was an apparent decrease of rubber in the shrub. There was a slight decrease of resins in the crude rubber, but not enough to make any appreciable difference in rubber quality. The total amount of crude rubber recovered per ton of shrub harvested decreased with an increase in the length of time of storage.

(2) Baled - defoliated. Shrubs stored after defoliation showed an increase in the percent of rubber hydrocarbon in the crude rubber, accompanied by a decrease in the percentage of resin. The insoluble content increased with increased time of storage. The total amount of rubber recovered in the crude increased somewhat up to the sixth week of storage, but dropped slightly thereafter. The total amount of crude rubber recovered per ton of shrub harvested increased slightly from the third to the sixth week.

For both types of storage there was a lack of uniformity of raw material into the mills and of the crude rubber recovered. These variations caused uneven drying and produced a final crude that was sticky.

(3) No storage. The rubber recovered from millings of freshly harvested shrub had Mooney values and molecular weights markedly higher than any rubber produced from the stored shrub. The lowered Mooney values and molecular weights are strongly indicative of rubber deterioration through oxidative processes. The amount of insolubles in rubber from freshly harvested shrub showed a marked reduction as compared to rubber obtained by conventional methods. Insolubles in rubber from freshly harvested shrub amounted to less than 50 percent of that usually present.

(4) Effect on rubber quality. It appears that two factors are present which have opposite effects on the physical characteristics of crude rubber recovered from shrub stored after defoliation. First, the physical properties of the crude rubber progressively deteriorate because of continued degradation of rubber hydrocarbon in the shrub during the storage period. Second, physical properties of the crude are enhanced by a depletion of resins during the storage period. For all physical properties measured, except Mooney viscosity, there is an apparent improvement in the quality of the crude rubber. The optimum improvement occurs at about five weeks. Deterioration occurs thereafter. Careful consideration of all the data indicates that the apparent improvement in the crude rubber is entirely due to a removal of part of the resins, and that there is actually a considerable amount of degradation in the rubber hydrocarbon present - and not an improvement as has sometimes been suggested. Removal of resins from rubber recovered from freshly harvested shrub (in which the rubber hydrocarbon had not been subjected to degradation)

by solvent extraction methods to produce a crude rubber with a resin content comparable to that produced from defoliate stored shrub would, as was later demonstrated, produce a rubber of superior qualities.

Investigations of storage of shrub to insure continuous mill operation are obviously not complete. So far as now known, shrub must be processed immediately after harvest in order to produce rubber of optimum quality.

Storage of shrub after defoliation has been and, more or less, remains a debatable question. In previous work, this form of storage has been termed "bale retting". Retting as such was excluded from further consideration in the current work because it is a microbiological process and as such presents several shortcomings. A "natural ret", that is,a ret induced by the mixed microfloral population present in the atmosphere, will probably vary greatly from season to season and from location to location. A pure culture ret would necessitate a costly installation to provide for sterilization of the raw material, maintenance of a pure culture inoculum, and apparatus for maintenance of the proper environmental conditions throughout the period of ret. It is doubtful if the price received for crude rubber could make a microbiological process as economically feasible in its production as could be expected from the production of an antibiotic such as penicillin. And last, retting at best removes only a small part of the resin and does not result in a rubber whose physical properties even approximate that obtainable by solvent extraction.

(5) Storage as ensilage. During the Emergency Rubber Project, a small amount of investigative work was done on the storage of shrub as ensilage under essentially anaerobic conditions. This work, meager though it was, gave some indications that shrub could be stored over rather extensive periods of time without loss of rubber. With resumption of work by the Natural Rubber Extraction and Processing Investigations Project, the Bureau of Plant Industry, Soils, and Agricultural Engineering set up an experiment to further study this method of storage. At the conclusion of the storage period, the shrub was turned over to the Bureau of Agricultural and Industrial Chemistry for milling and rubber evaluation.

The shrub was received in three "lots" identified as follows: Lot #1 was shrub which had been ensiled for six months in a "warm" place with no water added to supplement the natural moisture of the shrub. Lot #2 was stored under conditions generally comparable to those obtaining for Lot #1, except that the surrounding atmosphere was described as "cool". Lot #3 was material stored for six months under "cool" conditions with 25 pounds of tap water added to the lot.

Two different methods of handling the shrub were used. In one the shrub was given conventional control milling, paila, and scrub mill treatments. No shrub preparation treatment was given as this was completed prior to putting it down as ensilage. The exact method of preparation is not known. In addition to the conventional pebble milling, some rubber was obtained after deresinating the shrub from Lots #1 and #3. Specifically, this procedure was as follows: (1) the shrub was extracted with four liters of acetone passed through the shrub 5 times at room temperature. (2) The shrub was then extracted

with 3 liters of fresh acetone in 5 passes. (3) Step two was repeated with fresh acetone. (4) The shrub was rinsed once with 3 liters of fresh acetone. After this extraction, the material was pebble milled for 60 minutes at a water-to-shrub ratio of 4.5 to 1. The slurry was floated as usual and the rubber skimmed off. No paila or scrub mill treatment was deemed necessary. The wet worms were stirred in a furfural-acetone solution adjusted to a specific gravity of 1.0. After visual observation indicated the worms were clean they were rinsed with fresh acetone and dried in air.

Unfortunately, no records of weights of material into storage were maintained; consequently it was not possible to obtain yield data. All that could be obtained was an estimate of rubber quality as judged by certain physical characteristics. The optimum cure properties for the vulcanizates of the resinous crudes for each of the three lots are set out in the following table.

Table 1. Physical Properties of Vulcanizates of Resinous Rubber from Shrub Stored as Ensilage

Cured @ 287° F.	Lot #1	Lot #2	Lot #3
	p.s.i.	p.s.i.	p.s.i.
Tensile strength	1600	1435	1387
Modulus @ 600% elongation	455	335	380
Ultimate elongation	800	830	827
Hardness, Shore	29	27	28

These values indicate a decidedly poor quality rubber. The tensile strengths are far below that expected for the usual grades of resinous guayule while the hardness Shore is indicative of a very soft, plastic material.

Data for the deresinated material, as given below, show very little improvement.

Table 2. Physical Properties of Vulcanizates of Deresinated Rubber from Ensiled Shrub

Cured @ 287° F.	Lot #1	Lot #3
	p.s.i.	p.s.i.
Tensile strength	1980	1650
Modulus @ 600% elongation	900	700
Ultimate elongation	720	730
Hardness, Shore	35	33

The extent of improvement brought about by deresination is remarkable in its minimal effect. In both cases the vulcanizates were very slow curing. This may have been due, at least in part, to the formation of organic acids in the ensiling process. It was not possible at the time of this experiment to make Mooney viscosity or molecular weight determinations, but it may be hazarded that these values were both low.

c. Shrub Preparation. Parboiling and defoliation were generally accepted as desirable practices and were followed throughout the research discussed in the following pages. The topic of defoliation is discussed further in the section "Recommendations for Future Research".

(1) Cutters. During the life of the Emergency Rubber Project, considerable attention had been paid to the types of equipment needed to prepare the shrub for milling. At one time it had been contended that rotary fly-knife cutters (such as the Ball & Jewell or Sprout-Waldron) should supplant the use of crushing rolls. However, practical experience in factory scale operations indicated that maintenance costs for these cutters was excessive. Furthermore, even on the large sizes of cutters, the feed throat was so narrow that all means of automatic feeding of whole shrub proved impractical. Hand feeding resulted in exorbitant costs.

(2) Crushers and hammermills. Gradually the feeling grew that the use of any sharp-edged cutting device was not efficient in processing guayule. A conventional force-feed hammermill (Greundler Hay Grinder) was installed at Spence mill near Salinas toward the close of the Emergency Rubber Project. After minor modifications to strengthen the screen support at the point of entrance of the shrub to the milling chamber, this unit functioned with only minor maintenance to the close of the Project; and a similar machine would be recommended as the preliminary comminuting machine in any commercial operation now foreseeable.

It has not seemed feasible to eliminate crushing rolls from the mill circuit. The fact that the front and rear rolls turn at differential speeds and impart a "smearing" action to the rubber-bearing cells is highly advantageous in securing rubber release. In the event the latex in the cells is not already coagulated, coagulation occurs rapidly upon release of latex from the cells.

The effect of shrub preparation will be discussed in the section "Yield Studies". At this point it may be said that the only types of equipment for shrub preparation that would be recommended for inclusion in a factory would be some form of a continuous parboiler and defoliator, hammermills and crushing rolls.

d. Yield Studies. (1) Effect of shrub preparation. In the work done on the storage studies, it had been demonstrated that coagulation of the latex in freshly harvested shrub could be essentially completed by parboiling and subsequent mechanical treatment without the addition of coagulant chemicals. Recoveries in this work were about 90 percent of the available rubber hydrocarbon in the shrub (according to the method of chemical analysis then used as standard) under conditions that admittedly might not represent the optimum for maximum recovery.

Batch mill studies were carried out to determine the effect of additional mechanical treatment of the shrub after parboiling on the degree of coagulation of the latex, and upon the recovery of rubber hydrocarbon in the crude.

The first of these experiments involved extra crushing as compared to the standardized control milling. The results of this experiment showed rubber hydrocarbon recoveries in the control of 90.1 percent. Where the shrub had been crushed six times the recoveries increased to 98.5 percent. The mean difference required for significance at the 1% level was 5.4 percent. At the same time, the losses in the effluent, that is the rubber lost as latex, dropped from 5.7 percent to 1.4 percent. The least significant difference here amounted to 0.6 percent. Losses in the bagasse were 7.3 and 5.6 percent, respectively, but were not significantly different 4/. It was evident then that an increase in the amount of latex coagulated could be brought about by mechanical treatment.

In further experiments other methods of shrub preparation were tested. The results of these experiments are summarized in the following table.

Table 3. Rubber Hydrocarbon Recovered from Shrub Prepared in Various Ways (Mean values for the entire experiment)

Shrub Preparation	Hydrocarbon Recovery
	Percent
Crushed 2 times, hammermilled 1 time	90.8
Crushed 2 times, hammermilled 2 times	96.8
Crushed 4 times, hammermilled 1 time	97.0
Crushed 4 times, hammermilled 2 times	100.6

The difference required for significance at the 5% level is 6.2 percent. In this case, as in previous work, the residual rubber in the bagasse remained about the same for each method of preparation. Increased recoveries in the crude were due to a decrease in the losses of latex in the effluent.

All the work cited thus far was carried out by batch milling in 27-inch batch mills, and indicated that virtually complete recovery of rubber hydrocarbon was possible with this type of milling equipment.

4/ The consistency of excess rubber hydrocarbon accountability by chemical analysis of the mill products that indicates more rubber than can be shown by chemical analysis of the shrub (modified Spence-Caldwell method) has given rise to considerable speculation in the past. The success of chemical analysis of the shrub by then approved methods was based primarily upon extraction of the rubber from the plant material by suitable solvents. To say that batch mill balances were the best criteria for estimation of rubber available in the plant was to say that the mill products were more completely and readily extracted by the solvent in rubber analysis than was shrub material.

(2) Degradation by milling processes. Concurrent with the above work, some investigations were made to determine whether the rubber hydrocarbon was being degraded by the various processing steps. Degradation was judged by measurement of the molecular weight of the rubber hydrocarbon. A drop in molecular weight would probably indicate degradation by oxidation and chain cission. Briefly summarizing, it may be stated that none of the shrub preparation or milling processes resulted in a significant drop in molecular weight. Molecular weight of rubber in the shrub, as determined by an Ostwald-Fenske viscosimeter, ranged from 160,000 to 165,000. After the milling, values averaged 162,000. Following paila treatment and scrub milling, the average molecular weight was 157,000. This figure is not statistically significant. Drying at atmosphere in a circulating draft oven did result in a drop in molecular weight when the rubber was not protected by an antioxidant. The molecular weight of such rubber was 141,000 and this drop is significant. The maximum drying temperature employed was 200° F. Without going into the details here, it may be said that later work, when the rubber was protected by a suitable antioxidant such as "AgeRite White" and the maximum drying temperature was lowered, degradation to this extent did not result.

(3) From tube mills. In conjunction with the preparation of several thousand pounds of rubber for testing in aircraft tires, a controlled tube mill yield study was made. For this study, the shrub was given the optimum preparation compatible with the maintenance of steady production of rubber. The shrub, after being harvested, parboiled, and defoliated, was cut through the Papec and Ball & Jewell cutters. It was then crushed, hammermilled, crushed, hammermilled, and crushed in the order given. The feed rate was held as close as possible to the optimum rate previously indicated in exploratory experiments. These indications were that a feed of 100 to 125 pounds per hour (defoliated dry weight) gave close to the maximum yields obtainable. During the course of the yield study, which ran through 8 days actual milling, the actual feed rate was 110.6 pounds per hour. The total amount of shrub fed was 5,421.25 pounds, dry weight. The total amount of rubber hydrocarbon available, according to chemical analysis of the shrub, was 912.8 pounds. The amount actually recovered in the crude was 661.64 pounds or a percentage yield of 72.5 percent.

In this work the water-to-solids ratio was held to approximately 5 to 1. It was not possible, with the equipment and facilities at hand, to maintain this ratio without variation; however, ratios ranged between 4.5 to 1 to 5.7 to 1 at the entrance to No. 1 mill. Occasionally it was necessary to add a small amount of water at the transition between No. 1 and No. 2 mills. This was especially true early in the morning before the slurry had warmed up.

All the rubber produced in this yield study was floated across the rectangular flotation tank. The bagasse was discharged from the bottom of the tank then passed through a continuous centrifugal filter. Bagasse samples were taken at regular intervals and analyzed for residual rubber. Effluent was lost to the sewer at two points, i.e., from the mill sump and from the centrifugal filter. Sump losses of total effluent averaged 1,303 pounds per hour; those from the centrifugal filter averaged 1,938 pounds per hour.

Losses of rubber in the bagasse totalled 107.66 pounds or 11.8 percent of the rubber hydrocarbon available. Reflotation of bagasse samples in

battery jars failed to disclose any free floating rubber. Losses therefore must be attributed to rubber in the bagasse which was not released from the plant material by either shrub preparation or milling.

Combined losses of rubber from the sump and from the centrifugal filter were 16.75 pounds or 1.8 percent of the total rubber available. This gives a total rubber balance of 86.1 percent. The discrepancy must be attributed, in part, to faulty sampling and in part to the difficulty of making effluent analyses. Probably the greatest source of error in carrying out yield studies in tube mills is in attempting to decide exactly when to begin collecting data and when to stop. If the mills had been operated uniformly over several consecutive 24-hour periods, the matter would have been relatively simple. As it was, the exact retention time of material in the tube mills was never precisely established. It was observed in those cases where mill shut-down for several days was necessary, upon resuming operations again there was an overlap period of 2 to 3 hours when new and old material issued from the mill discharge. Consequently, on intermittent operation, the exact time when a given lot of material has passed through the mills must be estimated. An error of judgment at this point would offset the validity of interpretation of any yield data acquired.

The yield of rubber hydrocarbon as reported above, while not satisfactory, probably represents the most accurate analysis of tube mill yields that has ever been made - either in commercial milling operations or research wise. These yields point to the fact that tube mills may not be the best possible tool for the recovery of rubber, or that considerable additional work is needed to develop the optimum milling procedure.

(4) From jordans. In addition to this one study of yields from the tube mills, considerable work was done using a Noble & Wood "Baby" jordan as a milling tool.

In early laboratory or pilot plant investigations with small jordans, they were operated in a batchwise manner. Briefly, the procedure consisted of charging one of two vessels mounted above the jordan with a given quantity of prepared shrub (usually 5 kilos). To this was added sufficient water to make up a water-to-solids ratio of 5.5 to 1. The slurry was agitated with an air or electric mixer until the slurry achieved a consistency which it was believed would pass through the jordan. Then a quick-opening valve would be opened and the mass would be allowed to flow into the jordan as rapidly as possible. It would, after being passed through the jordan, be allowed to collect in the second vessel over the jordan. The slurry would then be passed through the jordan alternately from one vessel to the other with increasingly tighter plug settings until milling was judged complete.

As work progressed, it became evident that closer control and better results could be obtained if the shrub and water could be introduced directly into the inlet throat of the jordan. If this could be done, larger amounts of shrub could be handled at one time. This in turn, it was believed, would lessen the experimental error of the 5-kilo batches. A special feeder for this purpose was built. (See the section on "Machine Design and Development").

In the current work two jordans were available: one a Noble & Wood "Baby" jordan; and a Valley Iron Works machine of about the same size. In the Noble & Wood jordan the plug was about 14½ inches long, 13½ inches in diameter at the large end, and 9-3/4 inches in diameter at the small end. The blades, or bars, used were 1/8 inch wide, fitted onto the plug and shell, and held in place by wood filler blocks. The plug had 36 bars and the shell 84. The Valley Iron Works jordan was similar in design, but there were no wood fillers so that the bars formed rather deep channels on both the plug and the shell.

Believing it would be necessary to use progressively tighter plug settings, two wood tanks were set up to hold the slurries between passes. Each tank was equipped with an electric mixer to hold the slurry in suspension until it could be passed through the jordans again. The jordans were set up in series so that the slurry would pass through the first jordan (Noble & Wood) then into the second jordan and on into the first slurry holding tank, from whence it would return to the first jordan, into the second jordan, and then into the second slurry holding tank. The tanks were of such size that about 375 gallons of slurry could be handled at a time.

Early attempts to use this mill set-up were not very successful. It was not possible to provide sufficient agitation in the slurry holding tanks to hold the slurry in suspension. Furthermore, the second jordan plugged up very shortly after beginning a mill run. Each time it was opened up it was found to be full of milled out rubber. As the result of many trials with this particular mill set-up, the conclusion was reached that all milling could probably be accomplished in one pass in the Noble & Wood jordan if the proper techniques were used; and that, because of the absence of woods, the Valley Iron Works jordan would never be suitable for milling guayule. (Correspondence with the manufacturer had resulted in the information that internal alteration of the Valley Iron Works machine was not readily feasible.)

The Valley Iron Works jordan was pulled out of the line and work was concentrated on the Noble & Wood machine.

In the early work, while the development work on a suitable feed device was being done, it was noticed that if the feed rate was held down, milling appeared to be complete in one pass through the jordan. In other words, retention time in the jordan could be governed by the rate of feed. The jordan did not, as previously suspected, pump itself dry, but would put out slurry from the discharge only as fast as water and shrub were fed to the intake. As a result of these observations, the recirculation tanks were dispensed with and the slurry from the jordan was passed directly to a sump for dilution and flotation in all subsequent experiments.

While milling seemed to be complete in one pass, the action was very violent and it seemed possible that such drastic action might prove deleterious to the physical properties of the rubber. An experiment was run to get an idea as to rubber quality as judged by the Mooney value of the raw rubber.

Plants used were from a 7-year-old dryland planting of Variety 593 from Spence field. As soon as practicable after harvesting, the shrub was prepared in the standard control manner. Milling was done with the jordan set up

fairly close (until it sang). The feed rate was 134 pounds, dry weight, per hour. Shrub moisture was 33 percent. Water was added at the rate of 800 pounds per hour, though this varied somewhat due to fluctuations in water supply pressure.

The rubber was collected, decorked in the baica then scrub milled according to standard scrub mill procedure. From the scrub mill the rubber was arbitrarily separated into three lots or batches. These were deresinated by leaching with acetone in the following manner:- Each lot of rubber was spread out in a layer on the bottom of a screened-bottomed tray. The first lot was treated with 6 washes of fresh acetone using 2000 cc. per wash. The lots were allowed to stand 3 minutes in each wash and were drained for 1 minute between washes. The second lot used the last 5 miscellae from lot #1, plus one leach of fresh acetone as the last step. The third used the last 5 miscellae from lot #2, plus one leach of fresh acetone as the last step. All lots were allowed to stand in the dark at room temperature until dry. After the lots of rubber were dried, they were analyzed chemically and evaluated as to their Mooney viscosities. The results of the chemical analyses and Mooney values are tabled as follows:

Table 4. Characteristics of Deresinated Rubber from Jordan Millings

Composition	Batch 1	Batch 2	Batch 3
Ethanol solubles, %	2.84	3.44	4.00
Rubber hydrocarbon, %	93.87	93.17	92.36
Ethanol & benzene insolubles, %	4.66	4.52	5.19
ML 212° F. @ 5 minutes	96.5	92.5	93.0

From this it would appear that the violent mechanical action to which the rubber is subjected in the jordan is not deleterious to rubber quality. The Mooney values are in line with those obtained from the pebble-milled rubber. Such variation as is apparent is attributable to the variation in the residual resin in the rubber.

A good many experiments were carried out in an effort to get yield data which would be subject to reasonable interpretation. All of them failed because it was not possible to maintain a steady and constant flow of water required to make up the slurry. These variations in line pressure were due to heavy momentary drains by the baica. All regulating devices used did not correct the situation.

A system was finally evolved which gave fairly satisfactory hydraulic equilibrium. The system precluded the use of the baica for decorking, but did permit recirculation of water and recovery of all the crude rubber. All the water which went out of the system went out with the bagasse. Therefore the rubber shown to be present in the shrub by chemical analysis could be

balanced against that found in the crude rubber and that in the bagasse. Theoretically, this would permit a rubber accountability of 100 percent.

The system is described as follows:- Shrub was fed to the jordan together with the required amount of water. From the jordan the slurry was passed to a sump where it was diluted. The diluted slurry was pumped to a continuous centrifugal filter where the rubber, cork, and most of the water were separated from the bagasse. (It is worth noting here that most of the cork goes out with the rubber and water, but the centrifugal filter throws out more cork with the bagasse than does a conventional flotation system.) The rubber, cork, and water were passed from the centrifugal filter over a vibrating screen. The crude rubber and the cork which constituted the overs were dried in a tray drier after which they were analyzed chemically. The water and dissolved plant solids which passed through the vibrating screen were pumped to a surge tank for temporary storage. From this surge tank the effluent, as it was called, was pumped to the mill sump for slurry dilution and to the jordan where it was used as make-up mill water with the fresh shrub. The plant solids could build up to a maximum point where they would be thrown out with the bagasse. Fresh water was added only in amounts sufficient to replace that which went out with the bagasse.

A great number of experiments were run utilizing this system with considerable success. Total accountability of both total solids and rubber hydrocarbon was maintained with remarkable accuracy and reproducibility.

From the experiments carried out, it may be concluded that (1) milling in the Noble & Wood jordan did not give satisfactory yields of rubber hydrocarbon. Such yields ranged from 69.8 to 78.8 percent. The mean recovery was 76.25 percent. Total rubber accountability ranged from 92.8 to 103 percent. The average accountability was 97.9 percent. (2) Total solids accountability could be maintained with satisfactory accuracy and accountability. Such accountability ranged from 95.1 to 100.7 percent, with an average value of 98.1 percent. (3) Most of the losses consisted of unmilled rubber in the bagasse. Such losses ran as high as 21.6 percent.

(5) Varieties and hybrids. Yield studies were not confined to different modes of shrub preparation or to the use of such different milling tools as batch mills, tube mills, and jordans. Originally, it was planned to conduct similar studies on the different varieties and hybrids as they were developed by the cooperating Bureau of Plant Industry, Soils, and Agricultural Engineering. The development of the various strains did not occur as rapidly as anticipated, so that only one such test was carried out. Several strains were used in carrying out this study. Their history is outlined in Table 5.

Milling was carried out according to the standard control procedure except that a water-to-shrub ratio of 5 to 1 was used instead of 4.5 to 1. This was done because the plants were rather young, and higher water-to-shrub ratios had been found beneficial in the recovery of rubber from young shrub. Milling was carried out for 90 minutes instead of the usual 60 in order to insure obtention of all the rubber possible.

Table 5. Parentage of Varieties and Hybrids

Strain	Parentage	Chromosome Number	Age (Years)
D-65	♀ Guayule 593 X ♂ Stramonium 43700	90	3
D-118	♀ Guayule 42268 X ♂ Stramonium 43691	90	3
D-153	♀ Stramonium 43691 X ♂ Guayule 4268	54	3
D-155	♀ Stramonium 43691 X ♂ Guayule 4268	54	3
4265-I	Feral, from Durango, Mexico	54	3
4265-X	Selection from 4265 from Durango, Mexico	72	3
593	McCallum strain	72	3
Mariola No. 1	♀ (Guayule x stramonium) X ♂ Mariola	90	2
Mariola No. 2	♀ Guayule X ♂ Mariola	72	2

After milling, the rubber was deresinated by repeated leaching with fresh acetone until the miscella exhibited no apparent traces of extractable resin. The acetone remaining on the rubber was driven off at room temperature and the rubber analyzed and tested.

Milling characteristics of the different strains showed widely varying characteristics. The observed differences in processibility are discussed as follows:

Strain D-65. Wood fibers were very long. Small worms of rubber were observed after one hour of milling. Worms after milling was completed were a bright olive green color, very buoyant in the flotation tanks, though difficult to recover because of their fineness.

Strain D-118. Wood fibers long and stringy. Flower stems were profuse. No distinct worms discernible at the end of one hour's milling. At the end of the milling the worms were very small, bright green and difficult to skim because of their small size. Buoyancy was average.

Strain D-153. Long wood fibers. No worms apparent at the end of one hour. At the end of the milling period, the worms were exceedingly fine, dull olive green in color.

Strain D-155. Wood tough and fibrous. Much more difficult to handle than guayule. Flower stems profuse. No distinct worms at one hour. At end of milling the worms were exceedingly

small, difficult to handle, and dull olive green in color. Dried deresinated rubber not rubbery in texture; more like dried putty.

Strain 4265-I. Very difficult to defoliate. Wood fibers comparable to usual guayule. At the end of milling the worms were typical grey-green and about of usual size. Rubber very buoyant and floated more readily than most.

Strain 4265-X. Defoliation not difficult. Wood character ordinary. Worm characteristics same as for 4265-I and 593.

Strain 593. Wood fibers very much shorter than for any hybrid, but about the same as the two varieties of 4265. Worms formed at end of one hour milling, and at the end of the milling period exhibited normal characteristics.

Mariola hybrids. The total amount of material available from these two plants was so small that it was not possible to process it in the small batch pebble mills. Accordingly, it was milled in the attritor. At the end of milling, the rubber aggregates were very fine, not worm-like, and could not be recovered by conventional skimming.

The relative amounts of rubber hydrocarbon recovered by milling showed considerable variation. Recoveries expanded to a per acre basis are set out as follows:

Table 6. Potential Rubber Hydrocarbon Yield Compared with Actual Recoveries for Various Hybrids and Varieties

Strain	RHC Available per acre	RHC Recovered by milling	Percentage Recovered by Milling
	Pounds	Pounds	
D-65	275	176	64.0
D-118	317	289	91.1
D-153	122	42	34.4
D-155	155	72	46.5
4265-I	365	365	100.0
4265-X	476	470	98.7
593	294	231	78.5
Mariola X's	46	21	45.6

The apparent advantage of the comparatively high yields from D-118 and D-65 are misleading because of the small size of the worms which would make recovery in a factory operation practically impossible at the present stage of process research and development.

It should be noted that as the concentration of rubber in the shrub increases, the mill recovery (percentage-wise) increases. This is illustrated in the regression depicted in Figure 1. This tends to substantiate previous work which had shown a constant and apparently fixed loss of rubber hydrocarbon in the bagasse and effluent.

In conclusion concerning this test, it may be said that (1) preparation of the shrub occasioned no unusual difficulties. Strain 4265-I was difficult to defoliate. All hybrids that had one Parthenium stramonium parent had tough, long-fibered wood. (2) All hybrids produced very small worms that were difficult to recover in the flotation system. One hybrid (D-155) produced a dry deresinated crude that was not rubber-like in texture. (3) Highest per acre yields, according to these tests, might be expected from guayule strains 4265-I and 4265-X. All guayule hybrids showed less rubber per acre than any of the straight guayule strains; and guayule X mariola hybrids were the least promising of all strains tested.

(6) Slow milling studies. In April of 1952 an experiment was set up on a factorial design to evaluate mill speed and milling time on shrub that had received three different comminution treatments. These different treatments were (a) crush once and hammermill once; (b) crush and hammermill then recrush; and (c) crush and hammermill then recrush and re-hammermill. Two different mill speeds, 50 and 80 percent of critical, were used, each at four different milling times, viz., 50, 65, 80, and 95 minutes. The 24 millings required were randomized as to order of processing, and milled in sets of four each week over a period extending from April 14 to June 14.

The effects of the various treatments on rubber quality were also noted. All calculations for percentage recovery of rubber hydrocarbon, as well as mill balances, were based on analyses of shrub and mill products made by the shaker method then accepted as standard by the Project.

The shrub for each week's run was harvested, parboiled 20 minutes, defoliated, cut through the Papec and through the Ball & Jewell equipped with a 1/2-inch screen. It was then split into four samples, and each sample given the comminution prescribed for its position in the randomized pattern. All were held until the following day, then each was milled at the speed and for the time called for in the random pattern.

The rubber from each lot was given the normal paila and scrub mill treatments and then deresinated by the standard method mentioned elsewhere in this report. The rubber was dried over night at room temperature, weighed, and sampled for chemical analysis and Mooney value.

Bagasse and effluents were handled as in the standard control milling procedure.

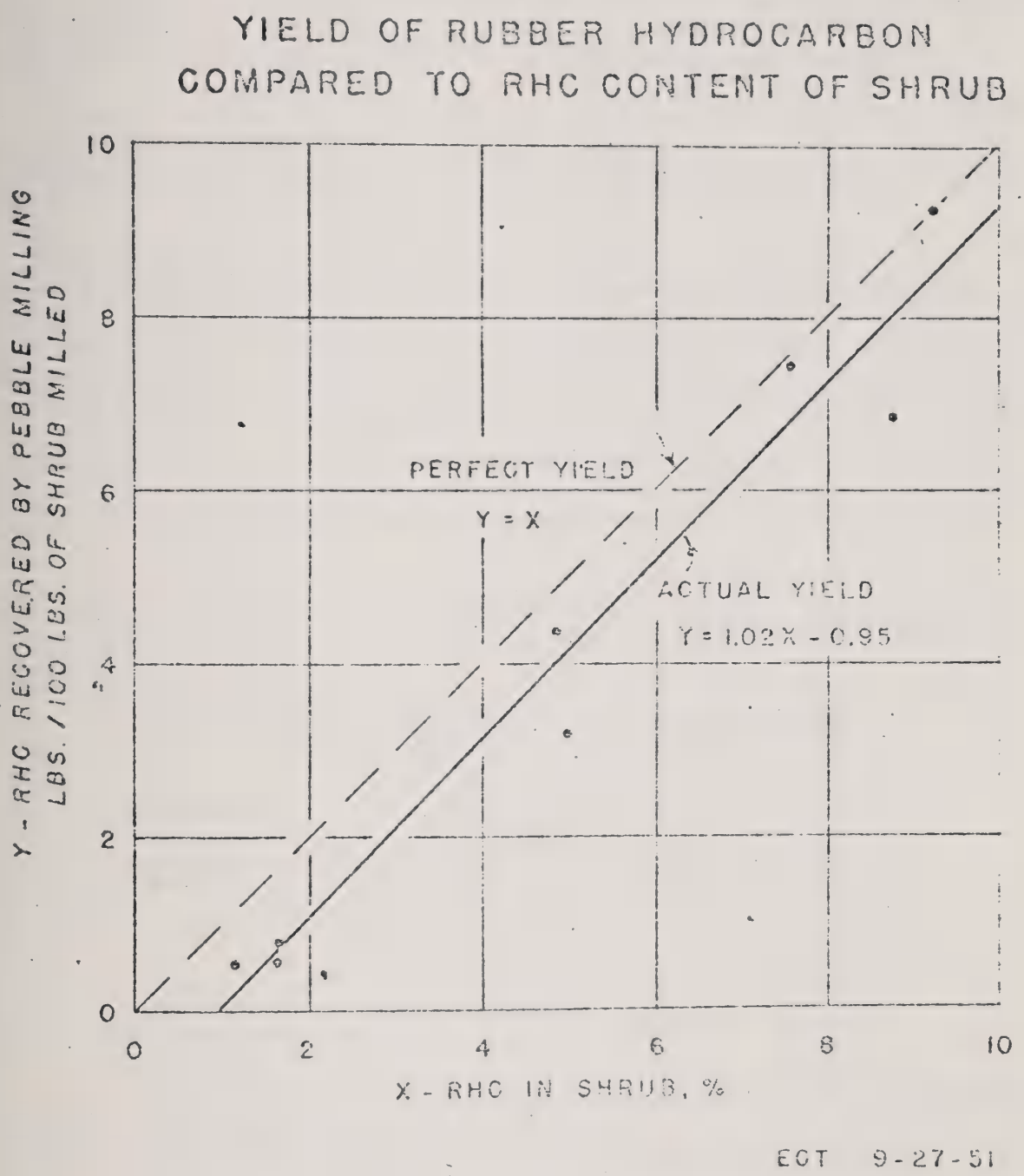

YIELD OF RUBBER HYDROCARBON
COMPARED TO RHC CONTENT OF SHRUB
Y - RHC RECOVERED BY PEBBLE MILLING
LBS. / 100 LBS. OF SHRUB MILLED
X - RHC IN SHRUB, %
PERFECT YIELD
Y = X
ACTUAL YIELD
Y = 1.02X - 0.95
0
2
4
6
8
10
ECT 9-27-51

Figure 1

The percentage recovery of rubber hydrocarbon for millings at 50 percent of critical speed averaged 81.42 percent; and 80 percent of critical was 83.04 percent. This difference is not statistically significant.

However, the increases in yields with increased milling time are statistically highly significant. The average yields for the various times being at 50 minutes, 78.63 percent; at 65 minutes, 81.04 percent; at 80 minutes, 84.35 percent; and at 95 minutes, 84.89 percent.

The yields also increase with increased pretreatment--the averages being for one crushing and one hammermilling 78.63 percent; for two crushings and one hammermilling 83.15 percent; and for two crushings and two hammermillings 84.91 percent. The least significant difference at the 5% level is 4 percent, indicating that the effective limits of pretreatment with the equipment in use was being approached with the second crushing. This is borne out by the fact that there is a highly significant difference between the rubber losses in the bagasse from shrub crushed and hammermilled only once and that receiving a second crushing. The second hammermilling had no further significant effect. These losses are, in the order of increased comminution, 7.79, 6.39, and 6.46 percent, respectively.

There are highly significant differences in rubber losses in the bagasse due to speed of mills, times of milling, and the speed x time interaction. This is shown in Table 7.

Table 7. Rubber Hydrocarbon Recoveries as Affected by Milling Speeds and Times

Critical Speed	Time Milled - Minutes			
	50	65	80	95
Percent	Percent Rubber Hydrocarbon Recovered			
50	11.15	7.64	5.72	4.48
80	8.16	6.74	5.20	4.70

Losses of rubber in the bagasse decrease with increased milling time. They are also greater in millings at 50 percent of critical than at 80 percent. The differences due to speeds disappear with longer milling times.

While mill speeds and milling times have no significant effect on rubber losses in the effluent, shrub preparation has a highly significant effect. The second crushing reduced these losses by 3.4 percent from those obtained from one crushing and one hammermilling. The second hammermilling made no significant further reduction. These losses, in the order of increased comminution, are 8.24, 4.93, and 4.79 percent, respectively.

There were no significant differences in resin content of the deresinated crude rubber due to any of the processing variations. The mean, and standard error, for the experiment was 2.59 $\pm$ 0.62 percent.

There were no significant differences in ethanol and benzene insolubles content of the crude rubber due to any of the processing variations. The mean, and standard error, for the experiment was 4.54 ± 0.51 percent.

There were no significant differences in ash content of the crude rubber due to any of the processing variations. The mean, and standard error, for the experiment was 1.63 ± 0.21 percent.

There is a significant correlation between Mooney values and resin content of the crude rubber. For each increase of 1 percent in resin content the Mooney decreases an average of 2.3 points. Inasmuch as the various milling treatments did not have any significant effect on the adequacy of deresination, the variations in resin content are considered as random results of the batch system used for deresinating in this experiment. The statistical evaluation of the effect of processing variations on Mooney values has been performed on Mooney values corrected to the average resin reading for the experiment. The differences in Mooneys due to shrub comminution are not significant.

Table 8. Effect of Shrub Comminution on Mooney Values

Comminution	Average Mooney
Crush 1 time, hammermill 1 time	93.7
Crush 2 times, hammermill 1 time	92.7
Crush 2 times, hammermill 2 times	93.1

There are highly significant differences due to milling time and speed of mills.

Table 9. Lowered Mooney Values Reflect Degradation of Rubber Hydrocarbon by Prolonged Milling

Critical Speed	Time Milled - Minutes 50	65	80	95
	Mooney Values			
50	93.7	95.2	92.7	91.3
80	93.5	93.8	90.3	89.7

The average differences between 50 percent and 80 percent critical speeds is 2.7 Mooney units.

Increased milling time decreased Mooneys an average of 1.4 units per 10 minutes of milling time.

Inspection of the Mooney data reveals markedly higher values for rubber produced from shrub harvested in June (the last 2 weeks of the experiment).

Unfortunately, the random assignment of treatments to milling dates resulted in all three 50-minute millings at 50 percent critical speed falling in these last 2 weeks.

e. Deresination. (1) Resin distribution and related characteristics. Guayule shrub, depending on its age and variety, contains from 5 to 15 percent of acetone soluble constituents, or resin. 65 to 70 percent of the total resin in the shrub is usually extracted by the deresination process, and this results in a reduction of more than 90 percent of the resin normally present in the crude rubber.

During the pebble milling process commonly used for the recovery of resinous rubber, part of the resin becomes incorporated with the crude rubber as a major impurity. In most cases, the crude rubber is found to contain about one-half of the total resin originally present in the shrub. Analyses of a large number of samples reveal that the ratio of resin to rubber hydrocarbon in the crude rubber obtained from freshly harvested, defoliated whole shrub is closely related to the ratio of resin to rubber in the shrub tissue. A similar relation exists with respect to partially deresinated shrub and the rubber milled from it.

When roots or branch tips of guayule shrub are pebble milled separately, however, somewhat different relations are found between resin-rubber ratios in the tissues of these parts and in the crude rubber. Essentially all of the root resin, for example, appears to combine with the rubber during milling since the resin-rubber ratios are not significantly altered by milling. Crude rubber recovered from the tips of guayule plants has a resin-rubber ratio lower than might be expected, judging from the relatively higher resin content of tip tissues.

These findings indicate that shrub tip resins are of a different nature, or at least in the pebble milling environment they behave differently than root resins do, because they do not combine so rapidly with the crude rubber during milling. Deresination of shrub by acetone extraction apparently removes the different types of resin of the whole defoliated shrub in the same proportions as initially present, as indicated by the constancy of resin-rubber ratios already referred to.

Crude rubber produced by the conventional milling process varies widely in chemical and physical characteristics. This is due primarily to the amount and kind of impurities trapped in the rubber during the milling, as well as the degradation of the rubber taking place during the so-called conditioning of the shrub to coagulate the latex.

The resin content of the crude rubber ranges from 20 to 35 percent and varies with the variety and age of the shrub, as well as the season of harvest, handling and pretreatment of shrub before milling, and other factors. Various methods of reducing this resin content have been tried with indifferent success. The rubber to be deresinated was obtained by conventional milling and usually was subject to degradation, sometimes severe, before deresination due to the conditioning treatments it received. Frequently the rubber thus produced was further degraded by drying before deresination. Very often in the

deresination process many fine worms floated in the miscella and were lost. Several solvents have been tried such as ethanol, acetone, furfural, glacial acetic acid, 2% sodium hydroxide in 95% ethanol, etc. While all of these reduced the resin content of the rubber, some of them had a deleterious effect - especially on the aging characteristics of the crude.

Thus, while the deresinated rubber was superior to the resinous rubber from which it was produced, it did not reflect the inherent quality of the guayule rubber.

Retting as a method of conditioning the shrub and reducing the resin content offered some improvement in the quality of the crude, but, as is pointed out elsewhere, the process was difficult to control and the resin content was rarely reduced below 15 percent.

The deresination of shrub as soon as possible after harvesting, by means of acetone, was first suggested as a method to coagulate the latex at the time when the rubber hydrocarbon is in its most uniform state and at its peak of quality. This could be performed under strictly controlled conditions without the degradation usually associated with heat or bacterial action during the conventional conditioning of the shrub.

During the Emergency Rubber Project, a small amount of rubber was produced by this method. Tests on this rubber indicated that a very high grade crude could be produced. At this time, both acetone and ethanol were used as solvents. Acetone was finally decided upon because it seemed to give better and more consistent results at room temperature. It also had a lower boiling point and latent heat, and could be separated completely from water solutions.

Investigations in the chemical laboratory in this connection indicate that somewhat different values for resin content of shrub and rubber samples are obtained, depending upon the choice of resin solvent. It was found that the shrub contains more ethanol-soluble than acetone-soluble material, but that the corresponding rubbers have either about the same or slightly lower values for ethanol solubles. The results are shown in Table 10. These findings are not surprising since the resin is known to comprise a mixture of many different constituents and cannot be considered as a definite chemical entity. They emphasize, however, the necessity of carefully standardized procedures of analysis to assure comparable values.

During the course of the work on control milling, it was discovered that the latex in freshly harvested "lush" shrub could be coagulated by parboiling followed by the mechanical treatment of cutting, crushing, hammermilling, etc. Crude resinous rubber produced under conditions governing the milling of lush shrub was uniform in quality and rarely showed any signs of deterioration.

Two methods of approach were now available for the production of crude rubber of uniformly high grade:--shrub deresination prior to milling and deresination of worms from lush milling. Each of the two methods offered certain advantages. To determine over-all superiority it was necessary to investigate both.

Table 10. Resin in Shrub and Crude Rubber as Determined by Acetone and Ethanol Extraction

Material	Number of Samples Analyzed	Resin Content by Acetone Extraction: Mean	Resin Content by Acetone Extraction: Standard Deviation	Number of Samples Analyzed	Resin Content by Ethanol Extraction: Mean	Resin Content by Ethanol Extraction: Standard Deviation
Fresh shrub	28	6.9	± 0.4	9	8.5	± 0.5
Deresinated shrub 1/	33	2.0	± 0.3	9	3.5	± 0.6
Crude rubber from fresh shrub	23	22.4	± 1.6	18	20.7	± 2.1
Crude rubber from deresinated shrub 1/	31	1.8	± 0.5	5	1.8	± 0.7

1/ Shrub was extracted with acetone in connection with laboratory and semi-pilot-plant-scale deresination experiments.

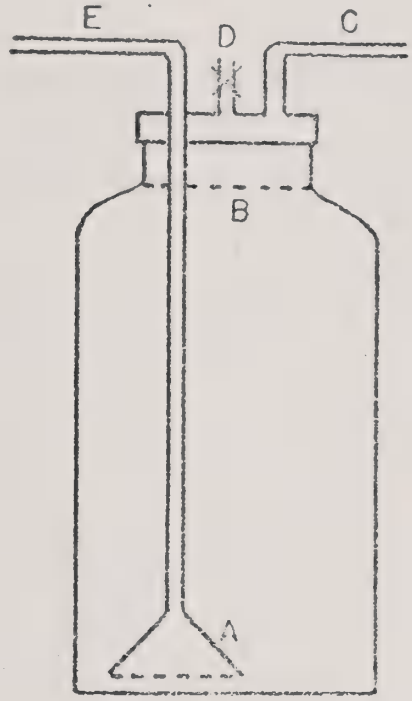
(2) Shrub deresination. The first studies of shrub deresination were carried out with shrub static in cells and the miscella flowing countercurrent to these cells. The apparatus used consisted of a series of 25 two-quart jars, each provided with a tube leading to the bottom and an outlet and an air vent at the top, as shown in Figure 2.

In setting up the series each "C" was connected to the "E" of the next jar. In the first step of the extraction miscella was introduced at "C" of jar No. 1, and the heavier water and resin solution removed at "E" of the last jar in the series, and cut into 2-quart fractions for use in succeeding runs. In the leaching step, the leaching miscella was introduced at "E" of the last jar, and the lighter acetone solution was removed at "C" of jar No. 1 and also cut into fractions and saved. A 40-mesh screen was placed over the opening of funnel "A", and another at the mouth of the jar "B" to prevent clogging of the tubes with shrub.

In operation, it was found that a gram and a half of fresh acetone per gram of shrub, following the last cut of miscella, was enough to complete extraction; while on the leaching step, four grams of water per gram of shrub, following the last cut of leaching miscella, completed the leaching.

After harvesting the shrub, it was parboiled 20 minutes and defoliated. The defoliated shrub was coarsely cut through an ensilage cutter, then by rotary knife cutter with an 0.5-inch screen, crushed by passing twice through crushing rolls with a 0.002-inch clearance between rolls, and finally hammer-milled through a 0.5-inch screen. This preparation was completed on the same day the shrub was harvested. Solvent extraction was begun the following day.

Each jar was loaded with 250 grams, dry weight basis, of the cut and crushed shrub. The moisture content of the shrub was adjusted to 60 percent



APPARATUS FOR
LABORATORY-SCALE
COUNTERCURRENT DERESINATION
OF GUAYULE SHRUB

Figure 2

by adding the proper amount of water where necessary for the sake of uniformity of different lots of shrub.

When the miscella had been used on six successive runs, it was considered that equilibrium conditions were well established, and each 2-quart jar of miscella was sampled. Analyses were made for content of acetone, resin, and water solubles.

The curves in Figure 3 show the water-soluble and resin concentrations attained in the extraction experiment, and the acetone content of the miscella at different stages. The different stages of extraction were arbitrarily divided into 100 theoretical stages for convenience and ease of presentation of the results.

Theoretical stages 1 to 66 inclusive cover the dehydration of the shrub and the extraction of resin with acetone; 67 to 100 cover the leaching of the shrub with water to recover the acetone.

The rapid and complete dehydration of the shrub (stages 1 to 66) and the sharp break in the curve (stages 67 to 100) from nearly pure acetone to a low acetone concentration are particularly noteworthy. Of extreme interest are the two high points in the resin concentration curve. This phenomenon has been evident in all the various miscellas produced and evidently denotes a partial fractionation of the extracted resins with respect to solubility in the advancing miscella. Between stages 15 and 20, miscella containing a high concentration of saponin-like materials was observed. The acetone curve illustrates the fact that there is no loss of acetone with either the outgoing miscella or shrub. In these runs, the ratio of miscella to shrub on the dry weight was of the order of 12 to 1, and good extraction was obtained in about 2 hours. Limitations of the equipment prevented investigation of shorter extraction times, and different miscella to shrub ratios.

After each of the six runs was backwashed, 2 jars were selected at random for analysis of the shrub, and the shrub from 20 jars was pebble milled for recovery of the rubber. The resin analyses of both extracted shrub and the rubber from each run are included in the mean values shown in Table 10. The chemical analysis of the rubber from the sixth run, for example, showed a resin content (as determined by ethanol extraction) of 1.66 percent; rubber hydrocarbon 89.70 percent; and ethanol and benzene insolubles of 6.58 percent.

Results of preliminary tests are shown in Table 11, wherein data for shrub deresinated rubber are compared with corresponding data for Hevea No. 1 Smoked Sheet and commercial resinous guayule rubber. Stress-strain values for the respective vulcanizates indicate that the shrub deresinated rubber approaches Hevea brasiliensis in quality

In the summer of 1950, 100 pounds of rubber from deresinated shrub were required for tests by private companies. To produce this rubber, semi-pilot plant scale apparatus was set up as follows: A battery of eight tubes 10-feet long by 5-inches in diameter was constructed of conductor pipe. These tubes were mounted vertically, and each was fitted with a device to provide a constant head for the introduction of acetone or miscella and a drain to provide semi-automatic operation. The design of these tubes is shown in Figure 4.

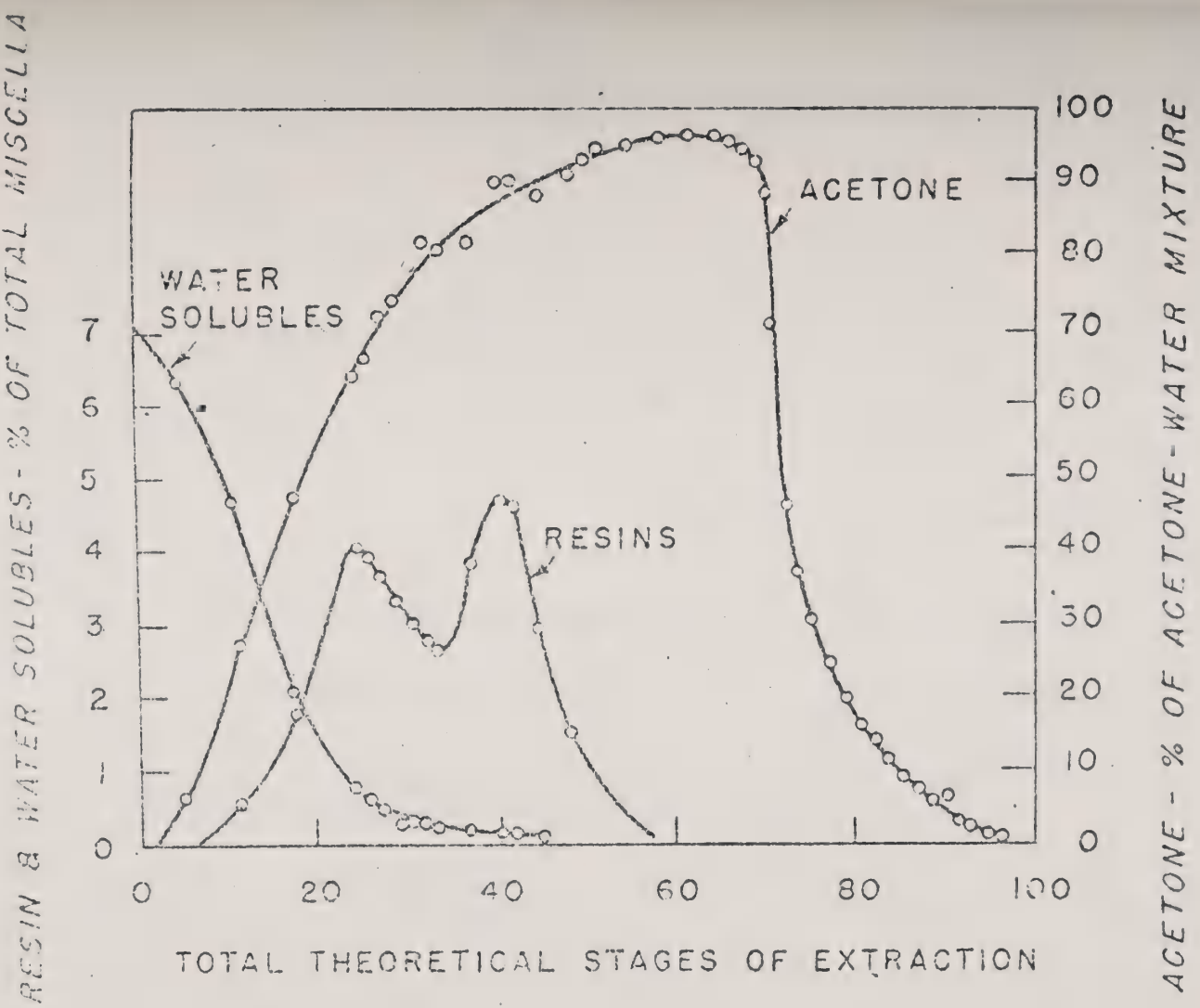
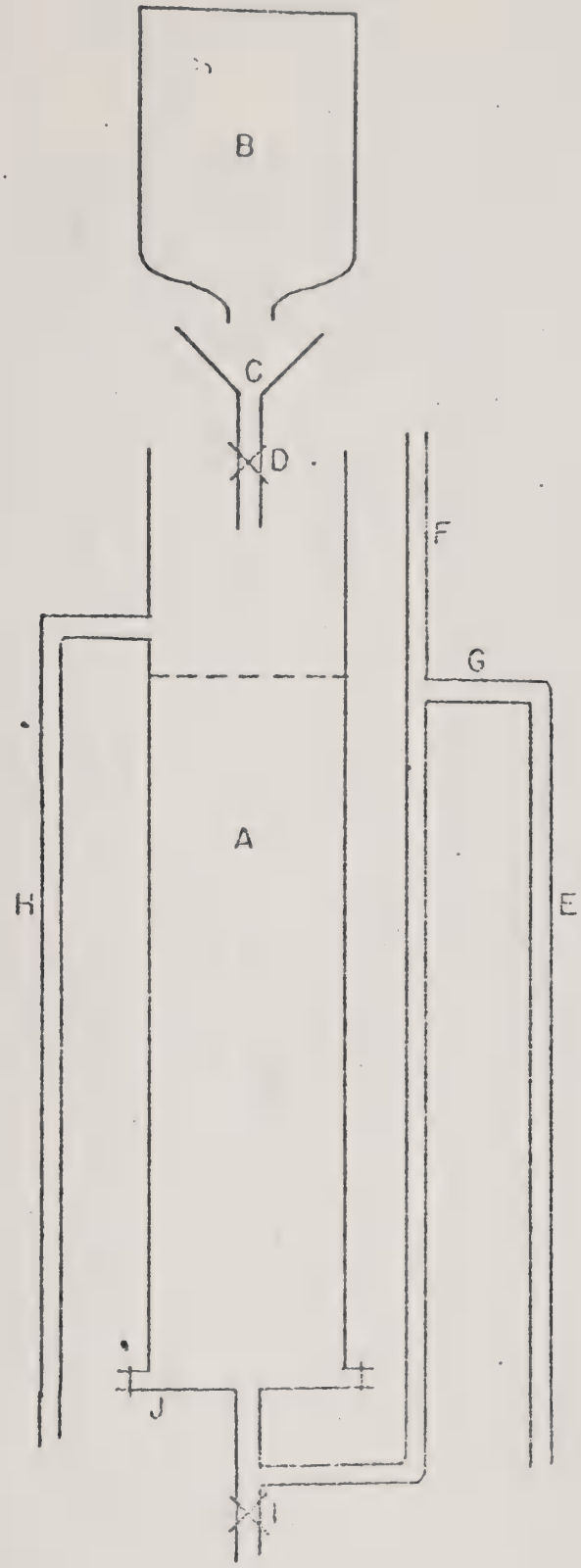


Figure 3

PROGRESSIVE COMPOSITION OF THE MISCELLA
IN COUNTERCURRENT DERESINATION OF SHRUB



EXTRACTOR FOR
SEMI-PILOT-PLANT-SCALE
DERESINATION OF SHRUB

Figure 4

Table 11. Comparative Results of Physical Tests of Shrub Deresinated Guayule Rubber, Resinous Guayule Rubber, and Hevea Smoked Sheet

Material	Mooney Viscosity ML 212° F. 5 minutes	Stress-Strain Data of Vulcanizates: Ultimate Tensile p.s.i.	Stress @ 500% Elong. p.s.i.	Stress @ 600% Elong. p.s.i.	Ultimate Elongation Percent	Elong. @ 400 p.s.i. Percent	Shore Hardness	Optimum cure time @ 287° F. minutes
Commercial resinous guayule rubber 1/	45 - 55	2500 -2700	350	--	800 - 850	--	25 - 28	--
Shrub deresinated guayule rubber	95	4060	830	1660	770	390	40	15
Hevea No. 1 smoked sheet	95.5	4620	865	1850	790	391	41	15

Formula: Rubber - 100; Stearic Acid - 4; Zinc oxide - 6; Captax - 1.0; Sulphur - 2.5; DOTG - 0.08.

1/ Average values reported by Place and Clark, in Emergency Rubber Project, using special guayule formulae.

The shrub used was prepared as in the preceding tests. Tube "A" was filled with the amount of this shrub normally used as a pebble mill charge. Bottle "B" containing acetone or miscella was inverted over funnel "C", and the flow rate regulated by valve "D". Maintenance of liquid level and withdrawal of miscella were automatic through pile "E" provided with anti-siphoning pipe "F". When extraction was complete, the acetone remaining in the tube was drained off through "I". Leaching with water to remove acetone from the shrub was accomplished by connecting funnel "C" to pipe "F", closing valve "G". Water and/or leaching miscella was introduced at "B" overflowing the acetone through "H". When leaching was complete, the water remaining in the tube was drained off; the bottom flange "J" removed, and the charge dumped into a container. As indicated in Figure 4, the extraction miscella flows downward through the shrub while the leaching miscella flows upward. These directions were chosen in order to minimize diffusion in the miscella by taking full advantage of the density differences of water, acetone, and mixtures of the two.

In operation, shrub moisture varied from 45 to 49 percent. As the miscella drained from the tube in each run it was cut into 5-gallon fractions and used in succeeding extractions, in the order of the cuts; the last cut of miscella was followed by pure acetone - approximately a pound and a half per pound of shrub. The first cut, approximately 5 gallons, consisted essentially of water normally present in the shrub. It contained no acetone and was not used in succeeding extractions. Two and one-half gallons of miscella were removed from the cut, where the resin concentration was 4 to 5 percent, to maintain the resin balance in the system. The acetone concentration in the miscella removed was 60 to 75 percent, equivalent to $1\frac{1}{4}$ pounds of acetone per pound of shrub. The difference between this figure for acetone removed and the $1\frac{1}{2}$ pounds added per pound of shrub is accounted for by evaporation in an open system.

When extraction was completed, the shrub was leached with water to remove the acetone by introducing water in the bottom and overflowing the miscella at the top of the tube, as shown in Figure 4. Cuts were also made in this miscella. These cuts were then used in the order taken for leaching succeeding extraction tubes. Analysis of the first cut showed that it contained 98 percent or more of acetone. This acetone was used to replace that which was carried by the shrub from the extraction step to the leaching step. It was added as the last cut in the extraction step of the next charge of shrub, together with the acetone used to replace that which was removed by the miscella in maintaining the resin balance.

A photograph of the battery of tube extractors will be found in the Appendix.

Some trouble was encountered with formation of precipitates in the backwash miscella, especially in those cuts where the miscella was rapidly changing from a high acetone content to a high water content. Removal of the water soluble material by leaching the shrub with hot water prior to extraction prevented the formation of these precipitates. Although this preliminary water extraction increased the shrub moisture from 50 to 75 percent, subsequent dehydration by the acetone miscella was readily accomplished, and the extraction of resin proceeded normally.

One hundred and forty-three mill charges were produced in this manner. Each mill charge of deresinated shrub was pebble milled 60 minutes at 80 percent of critical mill speed. The rubber was then given standard paila and scrub mill treatment, and was then dehydrated by immersing countercurrently in 6 cells of acetone--- the first cell being the second cell of the preceding charge, and the last cell being 100 percent acetone. The rubber was then sprayed with an acetone solution of PBNA in an amount calculated to leave 1% of the PBNA on the rubber. It was then spread on trays and dried at room temperature.

Approximately one-half of the first 50 charges in this campaign produced rubber which showed a high resin content and low Mooney values. These low values were caused by using one or more miscella cuts out of their proper sequence--one error, at times, being sufficient to affect the rubber of several succeeding charges. However, as soon as a definite procedure for maintaining the proper sequence was adhered to, the rubber produced was uniformly low in resin with a correspondinly high Mooney value. The average values for the last 91 of a total of 142 runs was Mooney 95.5 $\pm$ 3; and resin 2.89 $\pm$ 0.58 percent. This figure for resin is high by approximately the 1% PBNA added as an antioxidant.

Several types of apparatus for the continuous countercurrent deresination of shrub have been visualized; literature and patents pertaining to solvent extractors have been examined, but no suitable device has as yet been produced. The chief difficulties encountered are fines loss, bypassing of the miscella, and the maintenance of proper miscella to shrub ratios. Recent investigations, however, have indicated that proper countercurrent extraction conditions can be maintained on a moving perforated belt subjected to flooded percolation by a system of pumps, pumping from a series of tanks beneath the belt to sprays above it.

Due to the importance of other objectives, further investigations of shrub deresination were terminated at this point.

(3) Worm deresination. The existence of guayule rubber in the form of loosely aggregated, porous, spongy particles or "worms" (ca. 2-3 mm. x $\frac{1}{2}$-1 mm.) after pebble milling makes the rubber readily adaptable for the removal of its resinous constituents. Consideration of the properties of the resin solvents, described under resin distribution and related characteristics, led to the selection of acetone as the solvent of choice.

(a) Preliminary investigations. Accordingly, several preliminary experiments were conducted using acetone as the solvent in order to obtain some knowledge as to the extent of, and the time required for removal of the resins from the rubber. Investigations were made using C.P. acetone at 20°, 40°, and 56° C.; acetone containing 15%, 25%, 35%, and 50% water; and acetone containing 1%, 2% and 4% resin in order to determine the effect of these diluents on the rate and extent of deresination. Figures 5, 6, and 7 illustrate graphically the effect of temperature and the inclusion of water and resins on the rate and extent of deresination. The solvent to rubber ratio was made extremely large (115 to 1) to eliminate, for

EFFECT OF TEMPERATURE ON EXTRACTION RATE OF RESIN BY ACETONE

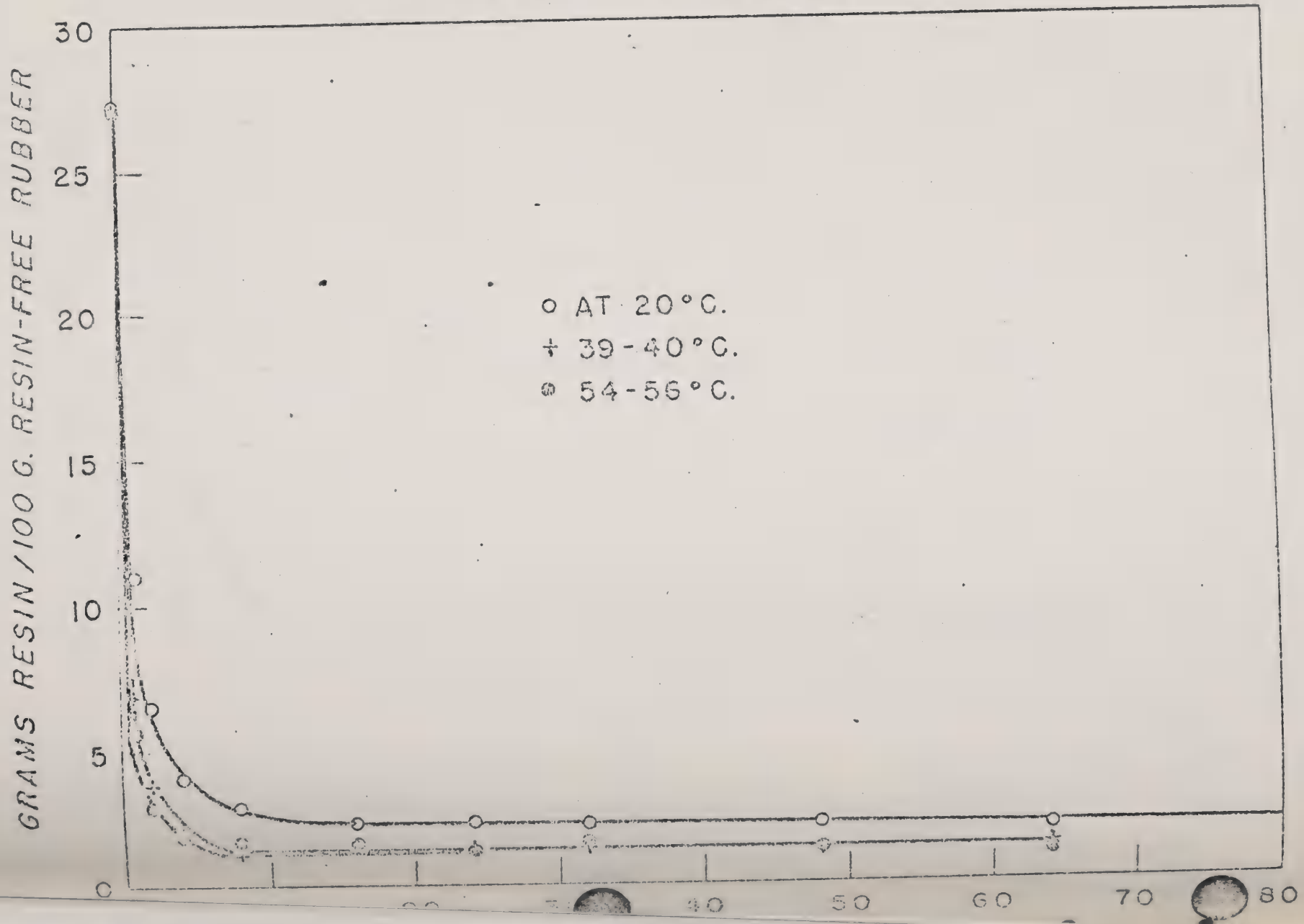


Figure 5

EFFECT OF WATER ON EXTRACTION RATE OF RESIN BY ACETONE AT 30°C.

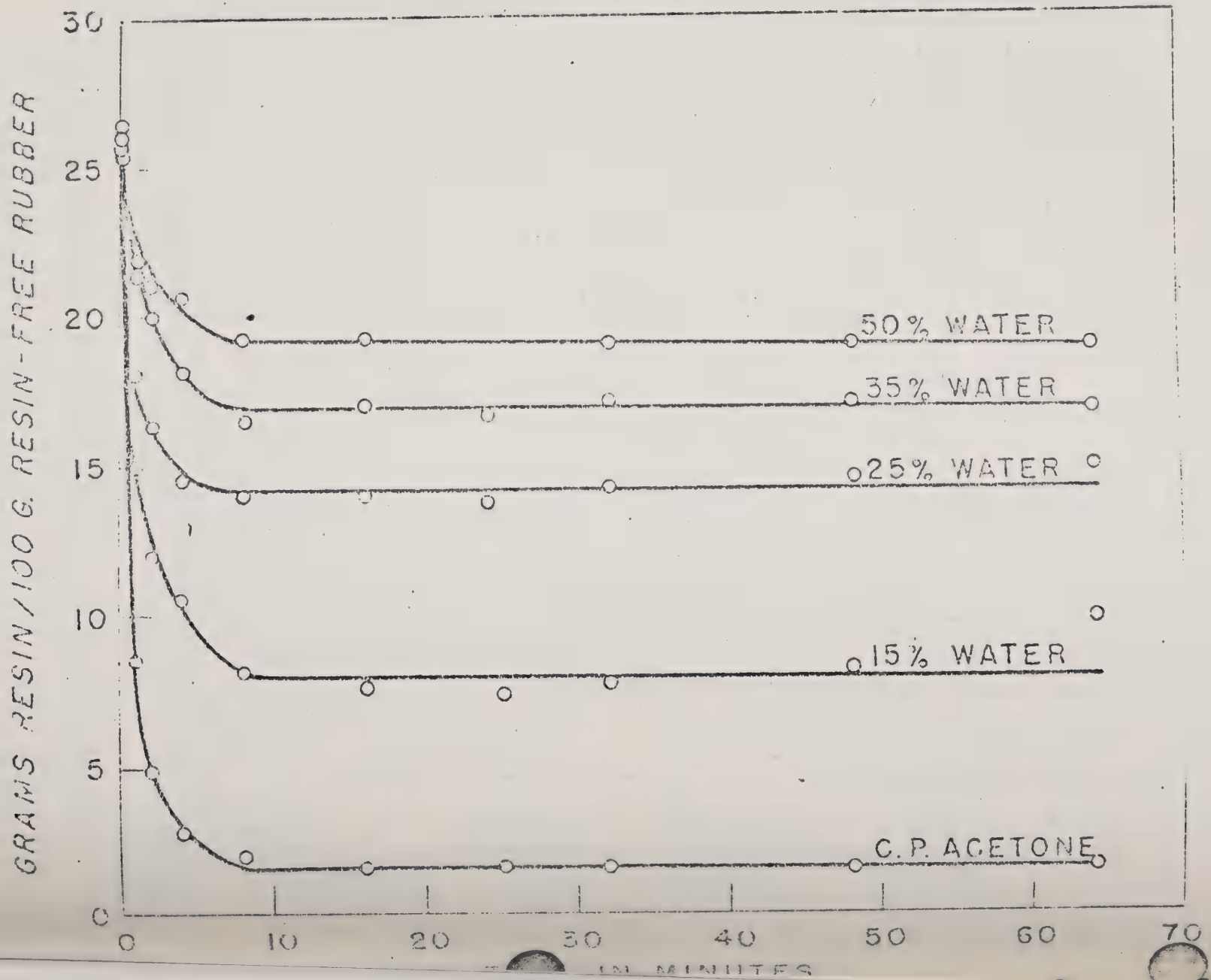


Figure 6

EFFECT OF ADDED RESIN ON EXTRACTION RATE OF RESIN BY ACETONE AT 30°C.

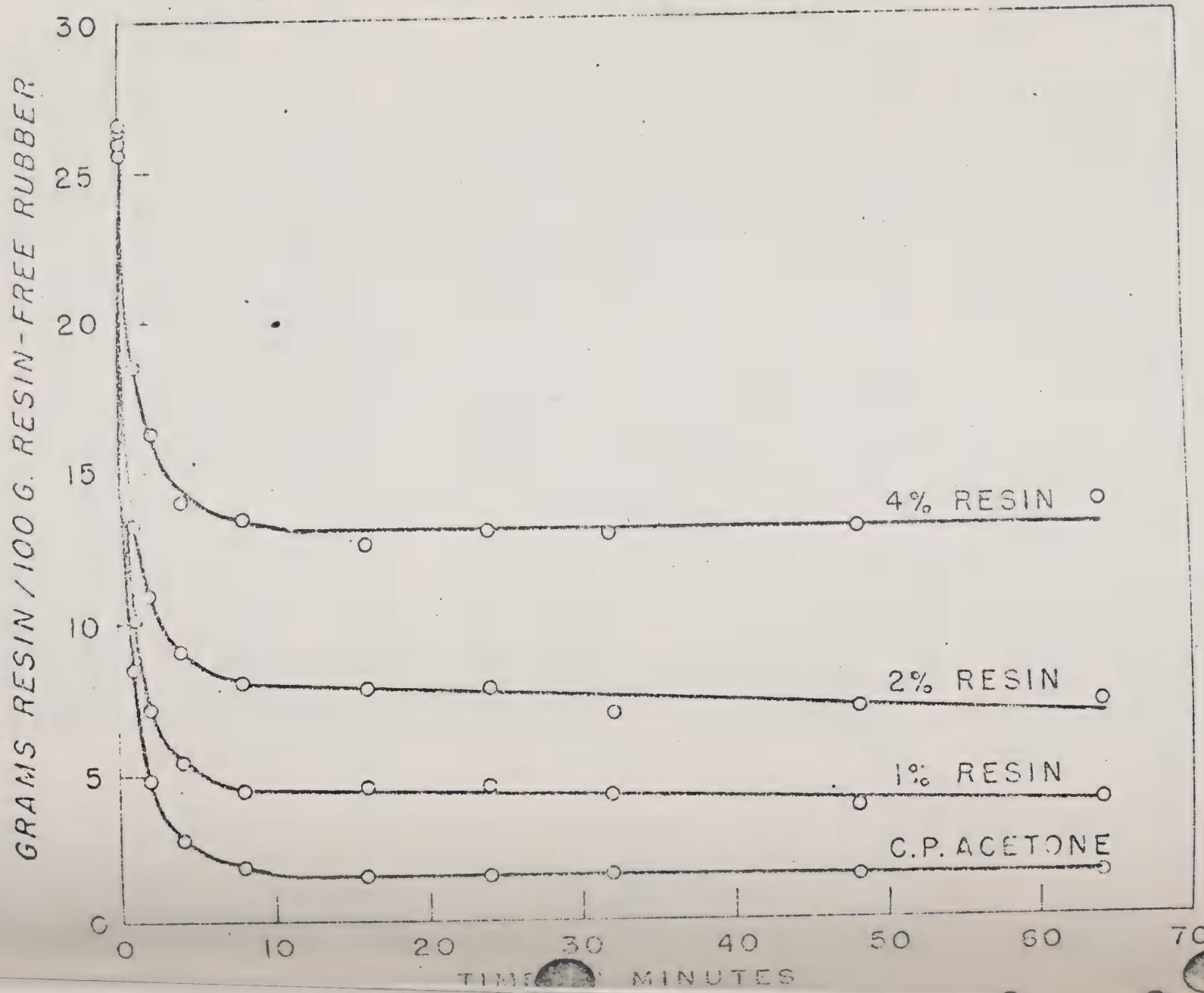


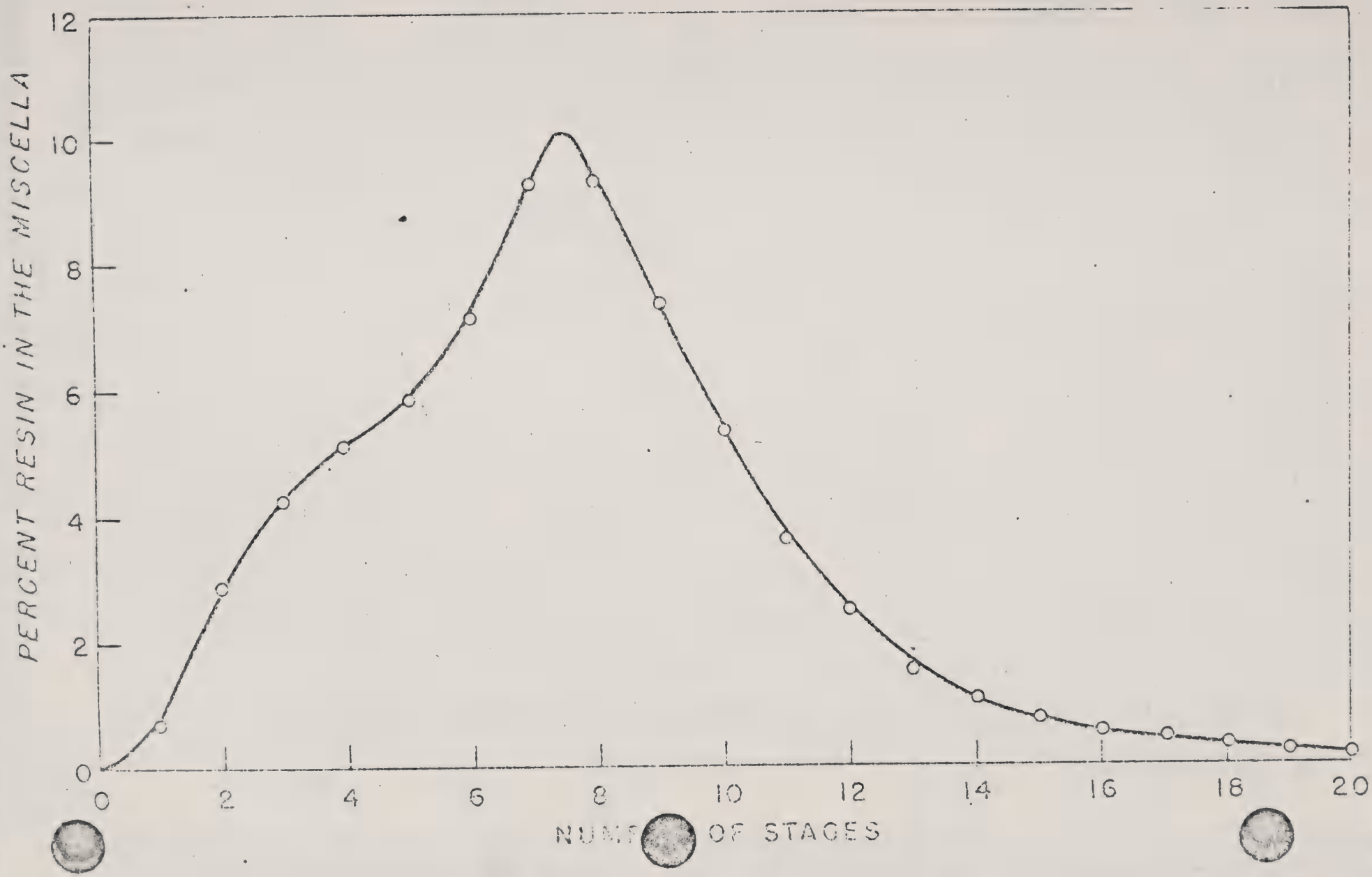
Figure 7

all practical considerations, the influence of the added water and extracted resin ($< 1\%$) on the course of the deresination. Starting with 110 grams of moist resinous worms (ca 56% moisture) containing 27 grams of resin to 100 grams of rubber (weight calculated on a resin-free basis), it was found that after 90 minutes of stirring the rubber worms in 7 liters of solvent at 20° C., the resin content dropped 98% to 2 grams of resin to 100 grams of rubber. Inspection of Figure 5 shows that after 2 minutes exposure approximately 76%, and after 3 minutes approximately 81% of the total resins were removed. After 90 minutes at 56°C., the resin content dropped 95% to 1.25 grams of resin to 100 grams of rubber. At this temperature, 2 minutes exposure of the worms in the solvent resulted in over 89% of the total resins being removed; and 3 minutes exposure resulted in the removal of over 95% of the total resins.

An inspection of the graph in Figure 6, depicting the effect that water exerts on the solvent power of acetone, shows that the presence of water does not affect the rate of deresination but markedly influences the extent of deresination. Figure 7, showing the effects of included resin on the solvent power of acetone, gives the same picture in regard to the effect on the rate of deresination. However, in interpreting the results shown, attention is drawn to Figures 8 and 9 which show that at a resin concentration of 2% in miscella containing essentially no water (stage 12), normal drainage of miscella of this composition from the rubber would result in a hold-up of $1\frac{1}{2}$ parts by weight of miscella to 1 part by weight of resin-free rubber. This would result in the deposition of 3 grams of resin per gram of resin-free rubber on the rubber sampled for analysis, so that the solvent power of acetone containing 2% resin is about 50% greater than that which would be inferred from an inspection of Figure 7. The same holds true for miscella containing 4% resin.

The next phase of research was an experiment designed to determine the number of stages and the equilibrium conditions prevailing in a countercurrent extraction procedure. This investigation was begun at a solvent-to rubber ratio of $2\frac{1}{2}$ to 1 in each stage. The results of this experiment showed that it was possible to obtain deresination in 20 stages while maintaining equilibrium at a peak resin concentration of 10% in the 7th stage. Figure 10 shows the grams of resin remaining on the rubber in each stage. It can be seen that deposition of resin on the rubber actually takes place in the first stages of the deresination so that more resin is found in the rubber up to and including stage 7 than is originally present. There are two factors which are responsible for this situation. One is the definite solubility limit of resin in acetone containing different amounts of water so that, as miscella

PROGRESSIVE RESIN CONTENT OF THE MISCELLA IN COUNTERCURRENT BATCH DERESINATION



PROGRESSIVE RETENTION OF WATER, ACETONE, OR MISCELLA BY RUBBER IN COUNTERCURRENT BATCH DERESINATION

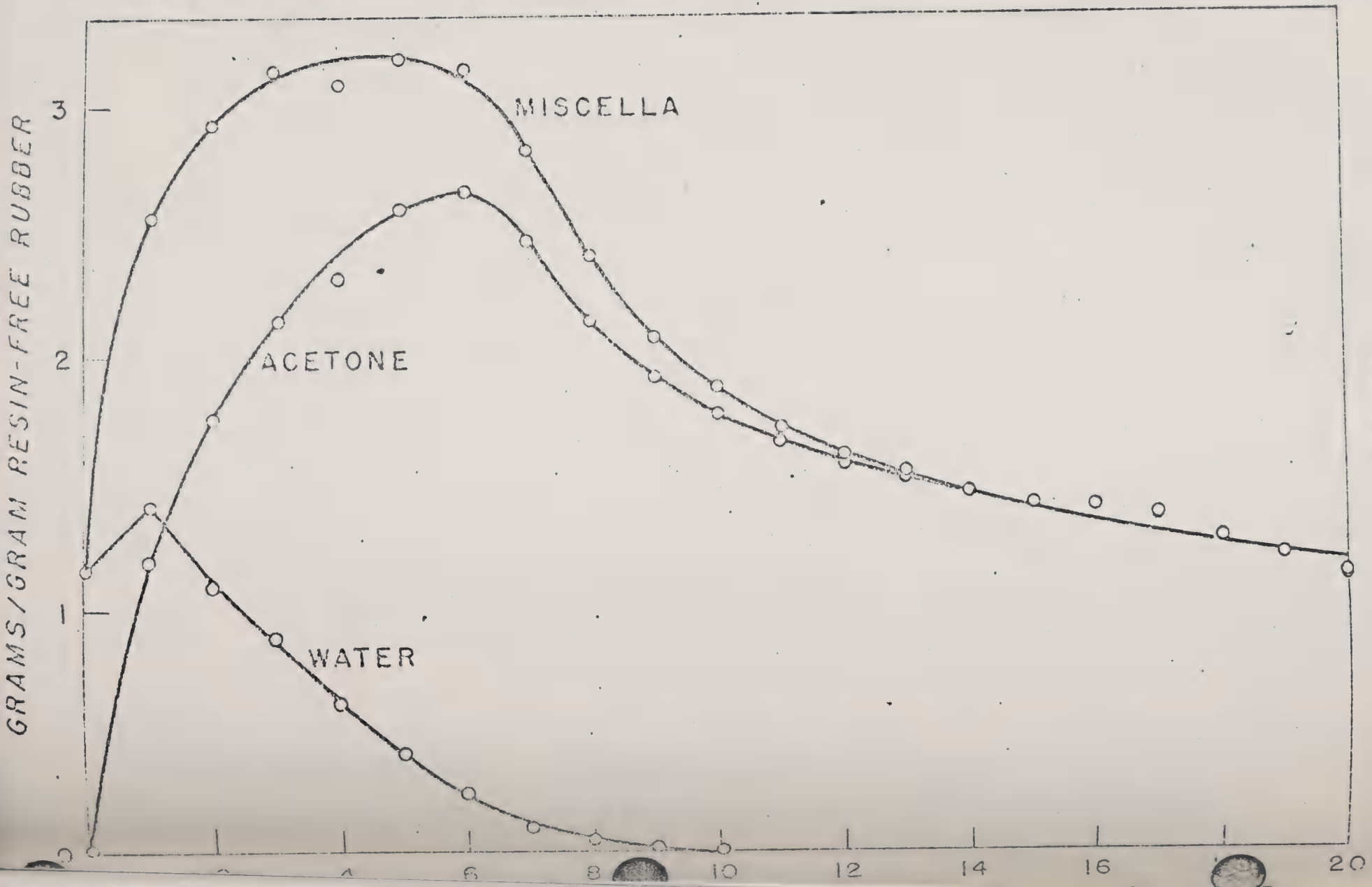
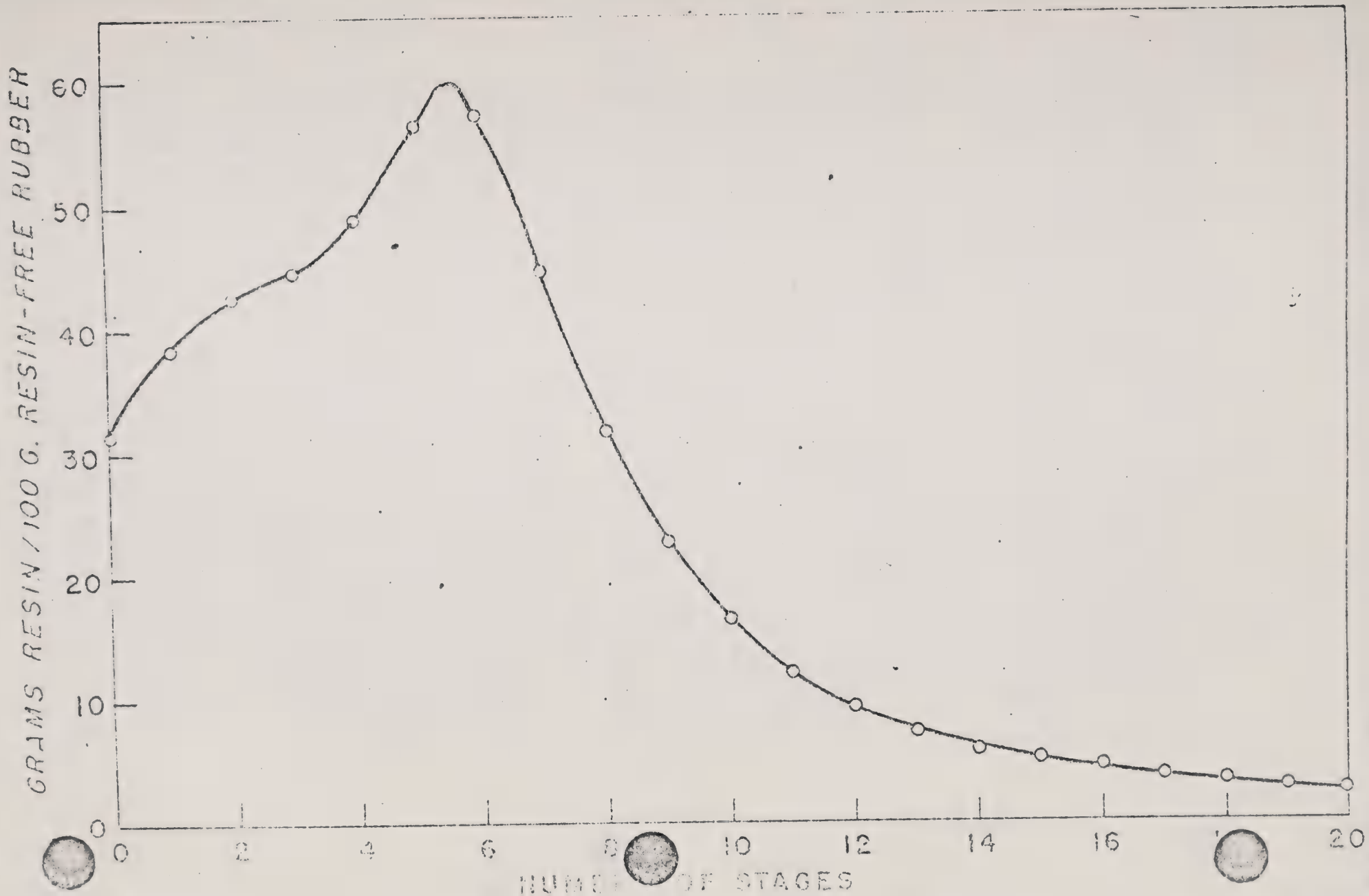


Figure 9

PROGRESSIVE RESIN CONTENT OF RUBBER IN COUNTERCURRENT BATCH DERESINATION



saturated with resin is added to freely drained rubber on which is retained miscella with a higher concentration of water, precipitation of resin on the rubber occurs. The other contributing factor can be seen by comparing the rise in retention ratio of miscella to rubber in Figure 9 with the practically parallel rise in resin value as is shown in Figure 10. Table 12 gives the water, resin, and acetone balances of this system calculated as grams per gram of resin-free rubber.

(b) Open system with agitation. In the spring of 1951, 4000 pounds of deresinated guayule rubber were requested for truck tire road testing. The apparatus used to produce this rubber was modeled on the laboratory set-up, and consisted of a 35-gallon stock pot with an opening at the bottom to allow drainage; a stainless steel 80-mesh screen basket, designed to contain the rubber, fitting inside the stock pot; and an air-driven mixer to stir the rubber in the miscella. After agitation, the miscella from each stage was drained into correspondingly marked solvent drums. The miscella from each run, with the exception of that sent to the recovery still, was re-used consecutively in the succeeding run. The miscella in each stage was pumped through a heat exchanger to a metering tank positioned above the stock pot containing the rubber, and then drained by gravity into the stock pot.

Certain modifications in the laboratory procedure were introduced in this system. The number of stages employed was reduced to 16, and the peak resin concentration of the miscella was adjusted and kept at an equilibrium value of approximately 6%. Redistilled acetone, approximately 95% pure, was added to the first stage, drained, and sent to the still for recovery. This served to remove the major portion of the water in the first stage, bringing the peak resin concentration into the sixth stage. The volume of miscella in each stage was 52 liters, with the exception of the first stage, which contained 72 liters of redistilled acetone. Miscella was removed from the first, second, and sixth stages to maintain equilibrium with the incoming water and resin.

An antioxidant, PBNA in an acetone solution calculated to leave 1% PBNA on the rubber, was added in the same manner as was the miscella, and drained. This solution of PBNA was re-used from one run to the next with acetone being added to make up any losses, and PBNA added to make up that which had been deposited on the rubber. The calculations for determining the volume and concentration necessary to deposit PBNA on the rubber by this method are based on a

Table 12. Water, Resin, and Acetone Balances for Laboratory Batch Deresination
(grams/gram resin-free rubber)

In	Grams	Standard Deviation 1/	Out	Grams	Standard Deviation
			Water removed in Stage 1 miscella	0.748	0.076
			Water removed in Stage 7 miscella	0.108	0.026
			Water removed in 1/3 of Stage 2 miscella	0.294	0.027
Water in wet worms	1.140	0.028		1.150	
			Resin removed in Stage 1 miscella	0.0086	0.0012
			Resin removed in Stage 7 miscella	0.2590	0.0147
			Resin removed in 1/3 of Stage 2 miscella	0.0215	0.0032
			Resin left in deresinated rubber	0.0244	0.0020
Resin in wet worms	0.314	0.010		0.3135	
			Acetone removed in Stage 1 miscella	0.608	0.038
			Acetone removed in Stage 7 miscella	2.430	0.131
			Acetone removed in 1/3 of Stage 2 miscella	0.471	0.015
			Acetone removed on deresinated rubber	1.299	0.010
				4.808	
			Acetone lost by evaporation and sampling	2.387	
Acetone added to system	7.195	0.839		7.195	

1/ The standard deviations were determined from the data of five runs made at equilibrium.

miscella to rubber ratio of 1.1 to 1 [5/]. This ratio is found in rubber below 2% resin concentration under free drainage conditions. After drainage of the excess antioxidant was completed, the rubber was removed from the stock pot and passed through a 1/4-inch screen in order to remove any lumps of underesinated rubber. The losses incurred were not measured quantitatively, but they were substantial. After screening, the rubber was dried for 2 hours in a circulating air oven at 40° C.

A total of 47 runs was required to establish optimum operating techniques, after which 170 runs were made in deresinating over 5000 pounds of rubber. A Mooney viscosity reading, ML @ 5 minutes, of 90 had been arbitrarily assigned as the minimum value for acceptance. On the basis of this standard, 41 out of 170 batches were rejected; the remaining 129 batches gave Mooney values of 93 ± 2; and an average residual resin content of 1.88 ± 0.32 percent.

During the first part of the production run, trouble was experienced with clumping of the rubber. At this time both a clothes wringer and a wine press were experimented with in an attempt to squeeze the water out of the rubber to reduce the amount introduced into the system. However, it was found that this resulted in the lumps of underesinated rubber appearing in the finished batch which had to be separated by screening. It was then found that rubber received from the scrub mill and held in stock pots filled with about an equal volume of water could be broken up more easily and handled better if the excess water were allowed to drain freely off the rubber. This resulted in more water being introduced into the system but did not measurably affect the equilibrium conditions. The resin peak remained at the sixth stage.

5/ An independent experiment, designed primarily to determine the distribution of water and resin in the miscella of a countercurrent extraction of wet resinous worms, gave additional information concerning the retention ratio of the weight of miscella to the weight of resin-free rubber in deresinated rubber at several levels of residual resin content. The solvent (acetone) was poured through wet resinous worms contained in an enclosed glass tube (122 cm. x 5.3 cm.), fitted with an inlet tube at the top and a regulated withdrawal tube at the bottom and inclined at an angle of 7° from the horizontal. The difference in weight between the wet deresinated worms after free drainage and after allowing the worms to dry gave the weight of miscella on the rubber. The weight of resin-free rubber was calculated from the weight of the dry deresinated worms, and an analysis of the residual resin content. At 1.75% resin content, the ratio of miscella to rubber is 1.04 to 1; at 3.11% resin, 1.086 to 1; at 6.49% resin, 1.207 to 1. A fairly good linear relationship is indicated here and the expression $y = .035x - 0.977$, where y = miscella retention ratio and x = residual resin content may be used for approximations throughout this range. This information concerning the retention ratio agrees fairly well with the data obtained from the foregoing experiment, as is evident upon inspection of Figure 9.

A considerable loss of fines accompanied the drainage of the miscella from the rubber in each stage. If this method of stirring the rubber in the solvent were used as a basis for a continuous deresination process, some method would have to be devised for fines recovery before the process would be economical.

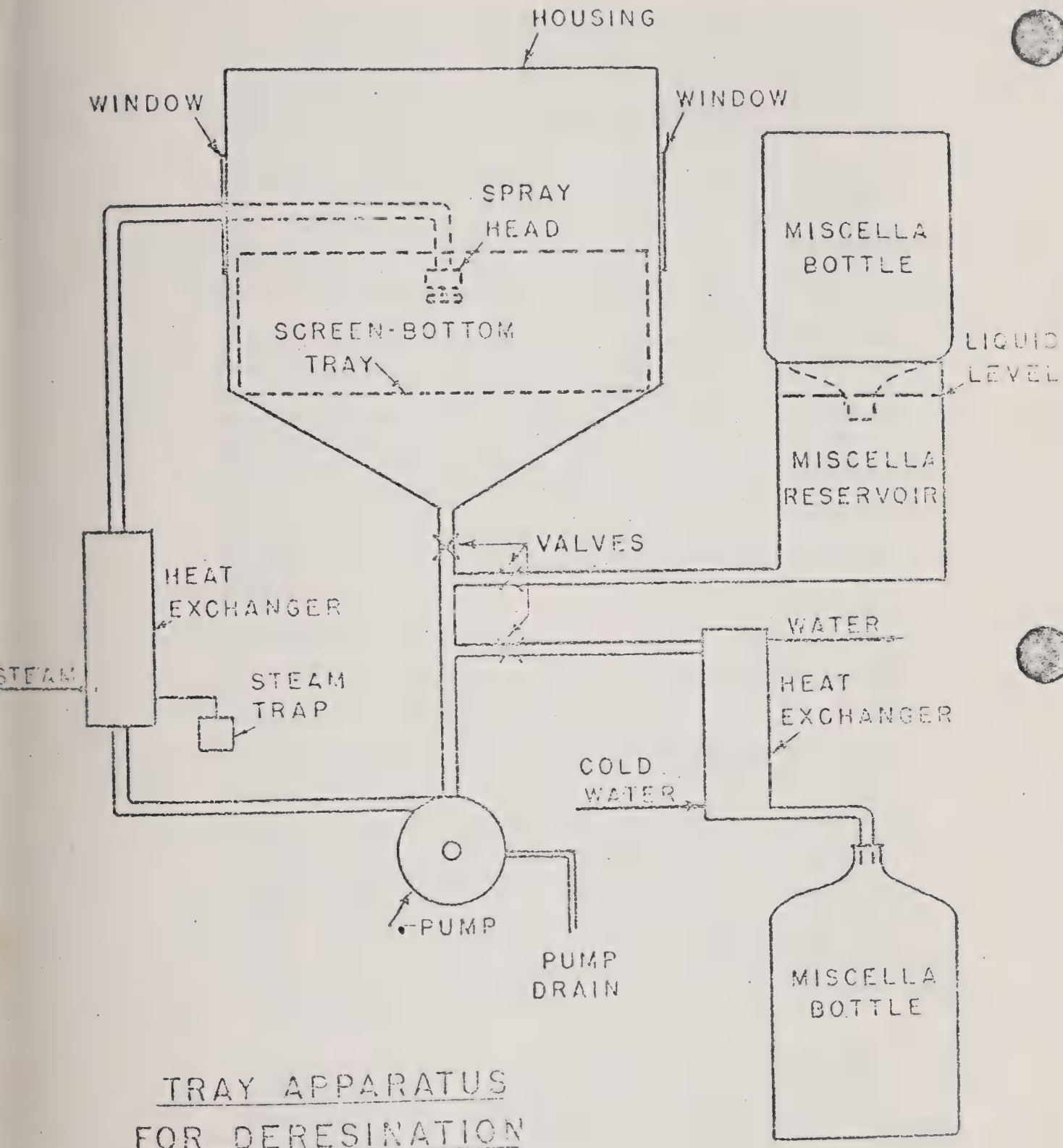
(c) Static bed extraction. Early in 1952 the need was apparent for a deresination apparatus in which all of the factors affecting deresination could be rigidly controlled. With such an apparatus, a standard procedure for deresination could be devised and the effect of changes in processing the shrub for rubber could be evaluated.

The apparatus developed is shown in Figure 11 and consisted essentially of a container 18" x 20" x 4" deep, with a screened bottom and with a spray overhead. This container fitted into a vapor-tight housing so arranged that the bottom drained completely into the suction side of a pump which circulated the miscella through the spray. When circulation was finished the miscella could be drained through a pipe line to storage containers or cells. A heat exchanger in the circulating line controlled the temperature of the miscella being circulated, and another in the drain line was used when necessary to cool the miscella to minimize vapor losses.

This apparatus could, in fact, be considered as one stage or section of a moving belt extractor (Wurster & Sanger continuous extractor). In operation, however, the bed was static and the miscella circulated by a pump was moved countercurrently by introducing the various cuts or cells of miscella in the proper order.

The procedure first used was to harvest and prepare the shrub for several batch extractions, or runs, as they are called in the remainder of this report. Then enough rubber was obtained by separate lush millings for each run as needed. This rubber was skimmed directly from the scrub mill flotation tank into the upper container. Later, rubber for several runs was milled out at one time and, after scrub milling, was held under water for use as needed during the following 3 or 4 days. For each run, enough of this rubber to make a bed approximately 2 inches deep in the container was weighed out and the clumps broken up with live steam. The worms thus separated were spread uniformly and without packing approximately 2 inches deep in the container 6/.

6/ No differences in Mooney values or in residual resins in the rubber could be detected due to differences in the two methods of milling, delay in resination after milling, or whether the rubber was skimmed directly into the container or steamed to break up the clumps.



TRAY APPARATUS
FOR DERESINATION
OF RUBBER WORMS

Figure 11

In the first run, 6 cells of pure acetone were used at a ratio of miscella to rubber for each cell of about 8 to 1. With each succeeding run, one cell or pure acetone plus enough to make up for the acetone carried out with the rubber and that lost by evaporation was added.

Sufficient runs were made to build the miscella to equilibrium at 25 cells. At equilibrium, cell No. 1 contained 85 to 90 percent water and the peak resin, 5.52 percent, occurred in cell No. 10. The system was kept in balance with the water and resin entering with the rubber by withdrawing calculated amounts of miscella from cell Nos. 1 and 9.

Enough runs were made to show that a standardized procedure described below could be adhered to readily and would produce adequate and uniform resin removal from beds of rubber produced under standard milling conditions. In these runs, no trouble was experienced with the loss of fine rubber through the screened bottom of the container. As the miscella was circulated, any fines which did pass through at first were filtered from the miscella by the bed of rubber itself. Rubber produced during these runs had an average Mooney value of 93.5 $\pm$ 2.5; and an average resin content of 2.81 $\pm$ 0.52 percent.

The standard procedure was as follows:

1. The rubber was skimmed directly onto the screen from the scrub mill flotation tank.

2. 25 cuts of miscella were used. These ranged in gravity from .980 for the first to .795 for the last.

3. After each extraction, miscella was removed from both cut No. 1 and at a later point, determined in each case by the specific gravity, where the acetone concentration was approximately 90%. The amounts of miscella removed at each point were calculated to be just sufficient to remove the water and resin added to the system by the rubber. These fractions were analyzed for resin and water so that adjustments could be made to maintain a uniform miscella throughout the experiment.

4. Each cut of miscella was maintained at a definite amount. Evaporation losses and the amounts removed for resin and water removal were made up from the succeeding cut. Enough fresh acetone was added at the end to maintain 25 fractions of miscella.

5. Each fraction of miscella was circulated through the rubber 2 minutes and allowed to drain 2 minutes.

6. The rubber was dried in a circulating air drier at room temperature.

(d) Design studies. At a later date, a series of experiments was run to determine more about the factors necessary for the preliminary design of a continuous countercurrent belt extractor.

Due to the limited time available, only a few of the many essential factors could be studied and no conclusive results were obtained. However, the results of six tests indicate that at temperatures of miscella ranging from 60 to 80° F., and using 97% acetone and 3% water, the resin in the rubber was reduced to 2.22 ± 0.31 percent. At 100° F. the resin was reduced approximately 1% lower to 1.29 ± 0.12 percent. There was no further appreciable reduction at temperatures up to 120° F. 7/. This 1% reduction in resin is accompanied by a sharp rise in Mooney value. Sufficient time was not available in which to determine by other accepted physical tests whether or not this rise in Mooney reflected an actual increase in rubber quality.

The rate of percolation of the miscella varied widely from run to run due probably to variations in the size of worms, density of the bed, and other causes. In each case, however, it was slowest at the point of highest resin concentration. Only one thickness of bed was investigated, viz., ca 2 inches. The approximate rates of flow through the bed are listed in Table 13.

Table 13. Rate of Miscella Percolation Through a 2" bed of Rubber

Concentration of Miscella			Rate of Percolation gal. per minute per square foot
Resin	Acetone	Water	
Percent	Percent	Percent	
3.5 - 4.5	85.6	10.0	.61
4.5 - 5.5	89.3	5.9	.46
5.5 - 6.5	88.5	5.6	.42
6.5 - 7.5	81.3	12.1	.38
7.5 - 8.5	85.3	5.9	.25

In order to establish the most economical maximum resin content in the miscella, these percolation rates would be a useful but

7/ The solubility curve of guayule wax in acetone at various temperatures might indicate that this reduction in resin may be due to the extraction of this wax at the higher temperatures.

not necessarily the deciding factor. Much would depend on the size and efficiency of the still for recovery of acetone, the ratio of miscella to rubber required in each cell, the type of worms received from the scrub mill, and other factors. The number of cells required would approximate 25. This number would depend on the maximum resin concentration deemed economical under equilibrium conditions, as well as the water concentration maintained in the first cell.

Listed in Table 14 are three sets of conditions which gave adequate deresination at room temperatures in our laboratory apparatus.

Table 14. Conditions to Give Adequate Deresination at Room Temperature

Water in Cell #1	Maximum Resin Concentration	Cell number of Maximum Concentration	Total Number of cells
Percent	Percent		
80 - 90	6 - 7	7 - 8	25
50 - 60	7 - 8	3 - 4	22
50 - 60	4.5 - 5.5	3	20

Each cell was circulated for 3 minutes and adequate draining time allowed to remove excess miscella. Water and resin concentrations were maintained by removing those amounts of miscella, calculated to remove all the water and resin that entered the system with the rubber, from cell No. 1 and the cell of peak resin concentration. As a control, checks by chemical analysis were made frequently.

The miscella to resin ratio for each cell was maintained at approximately 8 to 1 in all the runs made on this apparatus. In these studies, which were made at various times during an entire year, two different strains of guayule shrub of two different age groups (4 and 8 years) were used. The crude rubbers handled ranged in resin values from 20 to 33 percent.

The deresination process proceeded normally in all cases, as is shown in Table 15. In series 1 and 2, pure acetone was used. In series 3 and 4, 96.5 to 97.5% acetone containing 2.5 to 3.5% water was used. It is of extreme importance to note that deresination can be successfully accomplished by using acetone of 96.5 to 97.5% purity without recourse to acetone of higher purity. By reviewing the paragraphs

Table 15. Deresination of Rubber from Different Strains and Different Age Classes of Guayule

Series Number	Strain	Age in Years	Number of Samples	Season of Year	Acetone Concentration Used Percent	Original Resin in Crude Percent	Residual Resin Percent	Mooney Value
1	593	8	10	2/12 - 3/19/52	100	20 - 22	2.81 ± 0.52	93.5 ± 2.5
2	593	8	24	4/14 - 6/9/52	100	20 - 22	2.59 ± 0.62	94.0 ± 2.0
3	593	8	7	10/14 - 10/24/52	96.5 - 97.5	20 - 22	2.33 ± 0.47	---
4	4265	4	6	2/18 - 2/27/53	96.5 - 97.5	30 - 33	2.22 ± 0.31	99.5 ± 2.5

on solvent recovery it will be seen that the production of acetone of about 97% purity results in materially lower costs. The higher Mooney value of Series 4 may be due to the use of younger shrub, a different strain, or to factors so far unknown.

Besides showing uniformity in residual resin values between runs made under correspondingly similar conditions, flooded percolation showed uniformity across the mat of rubber. For example, for 5 positions on each of 14 mats, the pooled standard deviation was $\pm$ 0.24% resin.

Early in 1952 it was necessary to produce some 6000 pounds of deresinated rubber for further tests by private companies and in airplane tires. For this work a large deresinator, modeled on the small-scale apparatus previously described, was built and installed on a platform outside the pilot plant building. This deresinator held two trays with perforate bottoms (about 50% of the bottom area was open) 39½" x 42" x 4" deep. Each tray, when loaded to a depth of 2 inches, carried approximately 25 pounds of dry, deresinated rubber. Auxiliary equipment consisted of two metering drums for measuring the amount of miscella per stage; a bank of 25 drums for holding the various cuts of miscella; two pumps for circulating the miscella; a drum rack for new and recovered acetone; and a still for the recovery of acetone and resin from the miscella.

The operation of this apparatus was, in principle, essentially the same as that for the small-scale device. The rubber as received for deresination was obtained by standard tube milling procedure for lush shrub described elsewhere in this report. The rubber was cleaned up by scrub milling in 25-pound batches (as calculated on a dry, deresinated basis) - the rubber being floated from the scrub mill tank onto the deresinator trays. The trays were then placed in a holding tank filled with water at a level that kept the rubber floating within the deresinator tray. If the rubber had to be held for any appreciable time, the trays were covered to protect it from excessive exposure.

In the trial runs with the large deresinator, it was found that the rate of pumping the acetone out of each drum and circulating it over the rubber was too slow for a 25-cell system to keep up with the amount of rubber produced by the pilot plant each day. The decision to change the equilibrium conditions and shorten the system was based on the above consideration and on the finding that, since the deresinator was not vapor-tight, a considerable loss of acetone occurred during the circulation of the miscella. The amount of miscella that is withdrawn from the system determines the maximum resin concentration and other equilibrium conditions

under which the system will operate. The total amount of miscella that can be withdrawn per day and sent to the still for recovery is dependent on the recovery rate of the still. It was found that a 16-cell system containing 45 gallons of miscella per cell, and operating at a temperature of 32° C., was adequate to deresinate 50 pounds of rubber down to a residual resin content of approximately 2%.

The extraction system was originally started with 12 cells of 97% acetone, each cell containing 45 gallons of solvent. The resin and water content was allowed to build up and a fresh cell of acetone was added at the end of each run until the system had been built up to 16 cells. Samples were taken of the miscella from each cell after circulation over the rubber, and the percentages of total solids, water, and acetone determined. A study of the data accumulated showed that the cells containing the maximum resin concentration contained 85 to 90% acetone. Therefore the rubber was dewatered and the system shortened by adding 45 gallons of acetone as the first cell, circulating it over the rubber for 4 minutes, and allowing it to drain for 2 minutes. The resulting miscella was sent to the still for recovery of acetone and resin. The second and third cells from the previous run were likewise circulated and sent to the still for recovery. The fourth cell, after circulation, was returned to one of the two metering drums and losses that occurred during circulation were made up in the fifth cell after it had been circulated over the rubber. After bringing the fourth cell to volume, it was sent to the bank of holding drums where it became the second cell for the subsequent run. In the same manner, the fifth cell was made up to volume by the sixth cell and was then returned to be held as the third cell of the next run. The extraction was continued in this way, the volume losses in each cell being made up by the miscella of the following cell, to the 15th and 16th cells, which were made up with 97% acetone recovered from the still. Volume losses due to evaporation, sampling, spillage, etc., that occurred throughout the entire system during deresination, were also made up at this point by the recovered acetone. The 15th and 16th cells, after circulating over the rubber, became the 13th and 14th cells for the succeeding deresination.

Operating under these conditions, the maximum resin concentration found in the miscella was approximately 8% - occurring in cell No. 3 of the system. Twenty-five percent of the resin present was removed in the circulation and drainage of cell No. 1. The second cell entering the system removed no resin, but served to increase the percent of acetone in the miscella. Fifteen percent of the resin was removed in the third cell and an additional 15 percent was removed with the fourth cell. The fifth cell removed 12 percent of the resin so that in the first 5 cells of the system approximately 70% of the resin initially present in the rubber was removed.

An antioxidant was added by circulating a saturated solution of di-beta-methyl-para-phenylene naphthylamine (AgeRite White) in 45 gallons of 97% acetone over the rubber for 2 minutes, the temperature ranging from 20 to 25° C. Acetone will dissolve approximately 0.5% AgeRite White at 20° C. and, since slightly over half the weight of the contents of the tray after free drainage of the 16th cell was acetone, this proved to be a simple yet effective means of adding a uniform amount of antioxidant to the rubber without the necessity of exercising rigid control in making up the antioxidant solution. All that was necessary was to keep the solution saturated with antioxidant, and siphon off the supernatant solution as needed. It was found that this saturated condition was maintained by the addition of 1 pound of AgeRite White for every 3 batches (150 pounds) of dry deresinated rubber produced. An analysis of 228 samples for the percent of AgeRite White left in the rubber gave an average value of 0.47 $\pm$ 0.09 percent.

The rubber that was deresinated in the morning was dried initially for 2 hours in a circulating air oven in which the air, heated to 40 - 50° C., was forced through the rubber bed. Drying was completed by increasing the temperature to 65° C. for an additional 30 to 45 minutes, the drying time depending on the thickness and porosity of the rubber bed. The extent of drying was checked at intervals by taking the temperature in representative sections of the rubber bed by means of a thermocouple. The rubber deresinated in the afternoon was air-dried overnight and then dried at 65° C. in a circulating air oven for 30 to 45 minutes.

Fluctuations of $\pm$ 20% in the quantity of rubber received for deresination, variations in the worm size, tendency of the rubber to pack at different times, holding the rubber floating in the deresinator trays up to 70 hours before deresinating--- all these factors exerted only slight effects on the system and in the production of a high quality uniform deresinated rubber. The average and standard deviation of the residual resin content of 244 of the 25-pound batches was 2.10 $\pm$ 0.30 percent. The average and standard deviation of Mooney viscosity tests run on the same rubber gave an ML 4 5 min. of 96 $\pm$ 2.0.

Over 5000 pounds of rubber were deresinated by this method. Recirculating the miscella over the rubber took care of the fines problem completely. In only one 25-pound sheet out of 244 such sheets deresinated did the Mooney viscosity drop below 90.

(c) Solvent recovery. The still for reclaiming acetone and resin was a modified beer still designed for this specific purpose. The column was 2 feet in diameter by 12 feet high surmounted by another section 10 inches in diameter by 5 feet high. The whole column was divided as follows:

1. The bottom 36 inches contained a calandria 20 inches diameter by 24 inches long fitted with 100 one-inch I.D. tubes for a total of approximately 60 sq. ft. of heating surface.

2. The next 40 inches, packed with rocks 1 to 2 inches in diameter, was the stripping column.

3. Eight inches was unfilled and contained the feed distributor.

4. Forty-eight inches packed with rocks, also 1 to 2 inches in diameter, was a refluxing column.

5. Twelve inches of vacant space.

6. The top 10-inch x 5-foot section contained a copper coil and was used as a dephlegmator.

7. Vapors from the dephlegmator were passed through a water-cooled condenser.

Two air-operated temperature regulators were used for controls--one controlled the vapor temperature at the outlet of the dephlegmator by regulating the flow of water through the copper coil; the other controlled the temperature at a point 15 inches above the bottom of the stripping column, by controlling both the steam to the calandria and also the rate of feed of miscella to the still.

For continuous operation, the feed was introduced just above the stripping column at item 3 in the description above. The bottom section was fitted with a constant level overflow to remove water and resin, and to maintain the proper liquid level around the calandria. The still could also be operated intermittently by introducing the feed direct to the bottom section as required to maintain a proper liquid level.

As a stripping still, it was practically automatic in operation and would produce approximately 30 gallons per hour of 96 - 97% acetone. When acetone of a higher quality was required, this 96 - 97% acetone was re-run through the still operated intermittently. In this case, starting with miscella, about 100 gallons of 98 - 98.5% acetone could be produced in 6 hours.

The mixture flowing from the bottom of the still consisted of resin and an emulsion of water and resin--the free resin floating on top. This emulsion can be broken by acidifying and contains approximately 50% of the total resin recovered. This resin component is heavier than water.

Approximately 20,000 gallons of miscella were passed through this still at various times. No trouble was encountered with

resin plugging of the packing. It should be borne in mind that this apparatus was used for recovery of acetone only, but that similar characteristics would be expected with most other suitable solvents.

(f) Summary and discussion. It is apparent from the work done on deresination that rubber approaching Hevea in quality can be produced from guayule shrub in several different ways. Of these, flooded percolation on relatively thin beds of rubber worms from lush millings seems to give the most uniform and reliable results.

Guayule shrub can also be deresinated using the same method. In this case, however, more cells would be needed for the initial removal of water from the shrub; as well as for the removal of acetone from the shrub by leaching. Also, a separate set of cells would be required for the removal of water from the rubber produced after it was milled out of the deresinated shrub. The advantages of shrub deresination over worm deresination are: the possible recovery of water solvent materials in concentrations up to 10 to 12 percent in miscella in amounts up to 15 percent of the shrub; and the recovery of more resin which could possibly contain fractions not found in the resin from worm deresination.

While a great deal of deresinated rubber has been produced in both ways, very little has been produced from the same shrub by both means under comparable conditions. Consequently, no valid comparisons can be made as to the relative quality of the rubbers produced by shrub and worm deresination.

In either case, the amounts of miscella withdrawn from the system to maintain resin and water balances varies between wide limits. The acetone in the miscella, after removal of resin and water, is returned to the system.

In worm deresination, the ratio of the amount of acetone to the amount of deresinated rubber produced depends on (a) the resin concentration maintained in the miscella at the point of resin removal; (b) the concentration of water in the miscella at the point of water removal; and (c) the amount of water and resin introduced into the system with the crude rubber.

The conditions governing the acetone requirements would undoubtedly fall within the limits listed in Table 16.

In the shrub deresination process, the fresh acetone required is from 1.25 to 1.5 pounds per pound of shrub. With shrub averaging 15% rubber hydrocarbon the ratio of acetone to rubber for deresination would probably be between 8.5 and 10 to 1. This ratio would be increased somewhat if the acetone used in drying the rubber after milling were included.

Table 16. Theoretical Acetone Requirements in an Extraction System for Deresination of Guayule Rubber under Extreme Conditions

	Entering with Crude Rubber: Percent of Crude		Removed with Miscella (percent of miscella)					Acetone Required per Pound of Resin-free Rubber
			For removal of water 1/		For removal of resin 2/			
	Water	Resin	Water	Acetone	Resin	Water	Acetone	
Minimum	50	20	75	25	10	5	85	2.5
Maximum	70	33	25	75	5	5	90	14.0

1/ In dehydration stages.

2/ In extraction stages.

The use of acetone of a purity higher than 97% and temperatures above 100° F. seemed to offer no advantages.

The flooded percolation system produced uniform rubber under widely varying conditions of worm size, bed depth, time between scrub milling and deresination. Also, there was no loss of fines in the miscella or loss of rubber due to underesinated clumps of rubber. For these reasons, flooded percolation deresination of worms has proven itself far superior to any other method so far devised.

While several thousand pounds of high quality rubber have been produced, the methods of production used could in no sense be called a commercial process. In the development of such a process much pilot plant work remains to be done. Recent work has shown that the most promise for a successful machine for deresination lies in some sort of a moving perforated belt.

f. Latex Investigations. (1) Summary of Emergency Rubber Project Work. Emergency conditions of World War II prompted investigations of means for recovering latex from guayule, beginning in 1942, as part of the program for improving the quality of natural rubber obtained from this source.

Microscopic examination of guayule tissue reveals that the rubber is situated in non-connected cells, and also that approximately 95 percent of the rubber contained in freshly harvested undamaged shrub is in latex form. Treatments such as heating and desiccation of the shrub causes progressive coagulation of the latex. Exposure of cut or injured surfaces to air also promotes coagulation.

Mechanical rupture of all the rubber-bearing cells under proper conditions could conceivably result in complete release of the guayule latex into a liquid medium. It was on this belief that hope was based for development of a successful latex recovery process.

It was shown to be possible to disperse 85 percent of the rubber available in the shrub and then to recover 90 percent of that amount by centrifugation from the original dispersion. This resulted in an over-all net recovery of about 76 percent of the shrub rubber in the form of a concentrated latex containing 35 to 50 percent solids.

Guayule latex rubber showed physical properties and chemical composition superior to those of regular commercial guayule rubber. The composition of guayule latex rubber is quite similar to the composition of Hevea latex film, except that the latter rubber is slightly lower in resin and slightly higher in insolubles, according to analyses shown in Table 17. Attempts to develop a process for recovering a part of the rubber as latex and the rest as "worm" rubber were unsuccessful.

The physical properties of the vulcanizates were greatly influenced by the formula used. High tensile strength was developed only when sufficient

Table 17. Chemical Composition of Guayule and Hevea Latex Rubber

Composition	GUAYULE FILM		Hevea
	Young Shrub	Mature Shrub	Film
Hydrocarbon, %	86.0 - 88.0	89.0 - 91.0	88.0 - 92.0
Resin, %	10.0 - 12.0	7.0 - 9.0	6.0 - 8.0
Insolubles, %	0.5 - 1.5	0.5 - 1.0	2.0 - 4.0
Ash at 550° C., %	0.3 - 0.8	0.2 - 0.5	0.5 - 0.8
Nitrogen, %	0.1 - 0.4	0.1 - 0.3	0.5 - 0.6
Copper, ppm.	1 - 4	1 - 3	4 - 6
Manganese, ppm.	1 - 5	0.1 - 0.5	1 - 5
Iron, ppm.	20 - 40	10 - 30	50 - 70

accelerator and activator were included in the formula. Vulcanizates of guayule latex were characterized by lower moduli, higher ultimate elongation, lower permanent set, and slightly lower tensile strength than those of Hevea. Vulcanizates of guayule showed poor aging qualities unless antioxidant was added.

Work on latex was resumed in 1947 and was continued until June 30, 1949 at which time a 40% cut in appropriations necessitated elimination of this line of investigation.

(2) Work done by Natural Rubber Extraction and Processing Investigations Project. Work on latex recovery from guayule, since that done by the Emergency Rubber Project, was limited to the accomplishments during the period August 1947 and June 1949.

(a) Disintegration of shrub for release of latex. Disintegration of the plant cells of the shrub as the first processing step was generally accomplished by the use of a rotary knife cutter in the presence of water for initial reduction, followed by treatment in a pebble mill for maximum release of latex. Several experiments were conducted with an 8-inch Rietz disintegrator (a vertical type hammermill) to explore the possibilities of using this equipment for complete release of latex following the initial cutting treatment. The cut shrub was fed with added water at various rates, and various size screens were used. A maximum of approximately 87 percent of the total rubber hydrocarbon present in the shrub was released when the smallest size screen (1-1/6-inch) was used. However,

there was definite evidence of latex coagulation which is believed to result from the drastic action of the disintegrator and from the centrifugal action of the hammers which separated the added water from the shrub while undergoing disintegration. Similar experiments were also conducted with a 12-inch Rietz machine, but the results were less promising in that the percentage of rubber released was appreciably lower and considerable coagulation of latex was observed.

Results of research conducted under the Emergency Rubber Project indicated that when guayule shrub was processed during the active growing season, April through September, difficulties were encountered which rendered centrifugal concentration of the latex dispersions impracticable. The dispersions were unstable and coagulation of rubber took place within the centrifuge bowl during concentration, presumably because of the sensitivity of the latex to mechanical agitation. Undoubtedly some component of the leaves caused or contributed to this instability, since removal of the leaves before processing the shrub corrected the condition. In fact, dispersions produced from the whole shrub always appeared to be somewhat less stable than those prepared from the same lot of shrub after defoliation, regardless of shrub age or season of harvest.

Work was conducted during the 1948 growing season to evaluate the relative stability of latex as obtained from shrub growing under different soil moisture conditions, processed with and without leaves. Four-year-old shrub was processed by passage with added water through two rotary Ball & Jewell cutters in series, equipped with 1/4- and 1/8-inch screens, respectively. The resulting dispersions, from which coarse plant solids had been removed by means of a basket-type centrifuge, were concentrated by passage through the usual DeLaval latex separator. No pronounced variations in dispersion stability were detected in any case, even when the centrifuge was operated in such a manner as to favor latex coagulation by prolonging the retention time in the bowl. No satisfactory explanation exists for these results in comparison with previous observations. It can only be surmised that the experience gained in the extraction of latex from the shrub, and the subsequent handling of latex, had improved the over-all processing to such an extent that previously observed differences in stability were no longer apparent.

Analysis of the clarified dispersions of latex indicated the release of a larger quantity of water-soluble and dispersible materials when whole shrub was processed in comparison with defoliated shrub. The quality of the latex film rubbers, as judged by chemical analysis, seemed to be independent of shrub variables involved in those experiments.

(b) Removal of leaves. The fact that the shrub could be processed for latex during the active growing season without apparent difficulty simplified the process to the extent that it was seemingly unnecessary to remove the leaves. Nevertheless, it was considered desirable to defoliate the plants in order to reduce the amount of material to be handled, particularly the amount of finely divided plant solids which are dispersed in the latex. Since hand defoliation is impractical, and since parboiling treatment to effect leaf removal cannot be used in connection with latex extraction because heat treatment causes rubber coagulation, some chemical defoliation tests were conducted cooperatively by the Bureau of Plant Industry, Soils, and Agricultural Engineering in an effort to obtain further information relative to the feasibility of such a procedure, and its effects upon latex processing. Thus far it has not been possible to cause shrub to drop its leaves as a result of chemical treatment, although the leaves may be killed. Leaves are not readily removed in this manner because of the absence of an abscission layer.

(c) Centrifugation of latex. Cutting and disintegration of the guayule shrub in the presence of water, to effect release of the rubber in latex form yields a dispersion containing a suspension of plant solids together with the latex rubber particles. The suspended plant solids range from relatively coarse bagasse to very finely divided or colloidal particles. These solids must be removed from the dispersions by centrifuging in the course of recovery of the rubber. During these investigations, all centrifuging was accomplished by batch operation because no equipment was available which was capable of removing continuously the plant solids suspended in the latex dispersions. This limitation necessitated periodic stopping and cleaning of the centrifugal equipment.

A number of conferences and discussions were held with representatives of centrifuge manufacturers, with a view to designing a centrifuge capable of continuously discharging the fine plant solids which remain suspended in the latex dispersion after removal of the coarse plant solids, and at the same time capable of concentrating the latex. Such a machine (a modified Merco centrifuge) was designed and acquired for further process development; but only a few preliminary runs were made before curtailment of the latex investigations. These trials served to demonstrate that several modifications of the bowl parts, involving plate clearance and serum outlets, would be necessary before satisfactory separation of latex could be achieved in the manner as visualized.

Some experiments were conducted to determine the efficiency of separation of a DeLaval latex centrifuge (5-inch bowl) when operated at different dispersion feed rates and at

different bowl speeds. The data indicate that approximately 98 percent recovery of dispersed rubber may be attained at 9,000 to 11,000 r.p.m., with feed rates of about 400 ml. per minute. The efficiency of separation was lowered if the dispersion was allowed to stand until it became partially fermented.

A patent was granted for the development of a bowl modification on a conventional latex centrifuge. This modification consists essentially of a seal to prevent discharge of serum toward the cream outlet, and to prevent serum discharge other than that through a throttled serum outlet. The time which a rubber particle remains in the centrifuge is thereby controlled and clogging of the centrifuge by formation of solid or semi-solid masses of rubber is prevented.

(d) Aging of latex rubber. Sheeted cast film rubber obtained from guayule latex ages poorly by comparison with crude Hevea latex rubber. Since it is known that normal (whole) Hevea latex contains a substance or substances which serve to protect its rubber hydrocarbon, a study was made to determine the effect of adding Hevea latex serum constituents on the aging resistance of guayule latex rubber. Samples were exposed to direct sunlight and the relative extents of aging were measured roughly by the accompanying increases in acetone and alcohol soluble materials, decreases in molecular weight, and development of tackiness or stickiness.

Guayule latex to which had been added serum obtained from creaming Hevea whole latex was significantly improved in aging quality. Hevea serum obtained from centrifuged whole latex was somewhat less effective, but gave results superior to the untreated guayule latex. Hevea rubber freed from its serum ingredients was found to age poorly in comparison with the same rubber containing these substances.

(e) Cooperative tests. A sample of guayule latex was submitted to the Firestone Tire & Rubber Company for examination under the electron microscope. It was reported that few or no very small particles were found as compared with Hevea latex in which many particles of much smaller size are normally evident. It was also surprising to find no pictorial evidence of the approximately 15 percent of non-rubber constituents. It was suggested that these materials are either absorbed on the surfaces of the particles or are contained in the mass of particles.

Foam rubber samples were prepared from some of the latex rubber. Some difficulties in attaining compound stability and evidence of shrinkage were encountered in the preliminary tests, but a good product was eventually obtained.

g. Machine Design and Development. In addition to the lines of research reported on above, a certain amount of machine design and development work was carried out. The various items will be discussed in the paragraphs below in the order in which they would be used in a factory operation.

(1) Continuous parboiler. During the operation of Spence and Bakersfield mills during World War II, continuous parboilers were constructed and put into operation. These units were designed for handling whole bales and consisted essentially of a covered rectangular tank fitted with a conveyor for transporting the bales, and a heat exchanger to maintain the water at the desired temperature. These parboilers were not very successful for several reasons. In the first place, it was difficult to get penetration to the center of the bale---consequently defoliation was often incomplete. Secondly, there was no provision for handling broken bales so that a certain amount of material had to be prepared without defoliation or thrown away. Not infrequently bales broke inside the parboiler, which necessitated shutting down this phase of operations while a clean-out was effected. Heat exchangers were inadequate in capacity and the systems revealed many mechanical and operating shortcomings.

Facilities at the pilot plant were adequate on a batchwise basis for the amount of research and production milling that was required. However, it was recognized that the development of a successful continuous parboiler would be essential in any commercial operation. Preliminary design drawings were made for a continuous parboiler which would handle loose plants. The design envisioned a rectangular covered tank fitted with adequate steam heat exchangers. Provision was to be made for the automatic maintenance of adequate water supplies; for the removal of sludge which would collect in the bottom of the parboiler; and automatic temperature controls. Originally, it was believed that a double draper conveyor would be required, but further study led to the belief that a single top conveyor fitted with raker teeth would suffice. No materials were ordered and no structural work was done on the parboiler. Figure 12 is a schematic drawing of the parboiler design.

(2) Hammermill feeder. Very little machine development would be required for the shrub preparation phases of processing. It was believed that some comminution after crushing would be desirable to bring about complete coagulation of the rubber in the shrub. A hammermill appeared to be the best machine for this purpose, and was used extensively in this manner in process research and development. Commercial force-feed hammermills are available which will handle whole shrub satisfactorily; however, there do not appear to be similar devices commercially available which will handle shrub that has undergone preliminary comminution. A force-feed device was constructed which proved satisfactory. The hammermill available had the feed throat situated vertically at the top of the machine. To this feed throat was affixed a short vertical section of heavy gauge pipe of appropriate diameter. The upper end of this pipe ended in a cone-shaped feed hopper. In the feed hopper and pipe was installed a screw conveyor. In the cone-shaped section the scroll on the screw was extended as a series of arms which served to agitate the shrub in the hopper. The combination screw conveyor and agitator was powered by a gear head motor and an appropriate gear reduction unit. Comminuted shrub was fed to the conical feed hopper at a constant rate. The

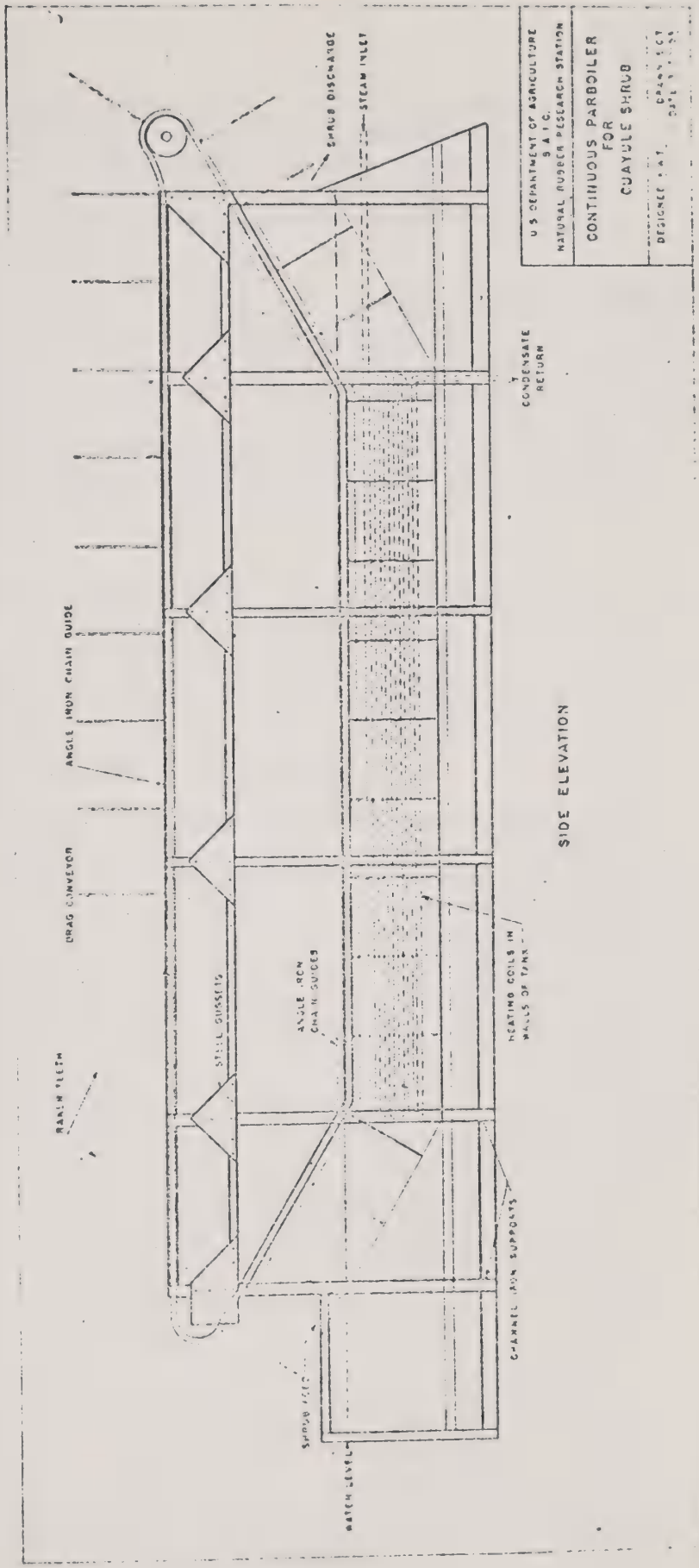

U S DEPARTMENT OF AGRICULTURE
S A I C
NATURAL RUBBER RESEARCH STATION
CONTINUOUS PARBOILER
FOR
GUAYULE SHRUB
SHRUB DISCHARGE
STEAM INLET
CONDENSATE RETURN
ANGLE IRON CHAIN GUIDE
DRAG CONVEYOR
RAKE TEETH
STEEL GUSSETS
ANGLE IRON CHAIN GUIDES
HEATING COILS IN WALLS OF TANK
CHANNEL IRON SUPPORTS
SHRUB FEED
WATER LEVEL
SIDE ELEVATION

Figure 12

screw conveyor forced the shrub continuously into the milling chamber. The unit was entirely successful and belies manufacturers' recommendations that hammermills not be used on moist or sticky materials. Variations in design and the use of multiple screw units would make such a feed device applicable to large-sized commercial hammermills equipped with either vertical or horizontal feed throats.

(3) Automatic bin discharger. A good many attempts have been made over the past 30 or more years to develop an automatic discharge bin for surge storage of comminuted shrub. It should be possible to discharge such a bin at controlled rates to provide a constant feed to a milling circuit. All such attempts have failed because they have not taken into full account the unique physical characteristics of comminuted guayule shrub. The material, especially when fresh, is moist and sticky and has an almost unbelievable propensity for packing and bridging. It has been known to bridge completely across a 14-foot bin.

During the research work carried out by the Natural Rubber Extraction and Processing Investigations Project, several additional types of bins equipped with automatic discharges were built, and the handling characteristics of the shrub investigated. None of these was entirely satisfactory but, as a result of this work, preliminary design work on what is believed to be a suitable automatically discharging bin has been completed. A schematic drawing of such a bin is shown in Figure 13.

Certain salient features of this type of bin deserve special mention here. For example, it will be noted that all four walls of the bin are inclined slightly from the vertical so that the bin is somewhat smaller at the top than at the bottom. Because fresh guayule shrub will cling readily to a vertical surface, it is believed this tapered construction is necessary to prevent bridging. The use of bin vibrators has not prevented bridging. The screw conveyors which make up the discharging floor of the bin limit the dimensions of the bin in their longitudinal dimension. Screw flights should not be longer than one standard flight. Two or more flights joined by hangers and bearings simply will not pass guayule, and such features must be eliminated in any construction. It is suggested that the use of such a bin as a source of feed for the mill circuit could best be accomplished by hooking up the drive mechanism to a weighing and controlling device such as a "Merrick Weightometer." If this system were to be used, the mechanical hook-up should be as close as possible to reduce the time lag between control and change of feed rate to the minimum. The weighing and controlling device could also be utilized to govern the addition of water to form the mill slurry. Here, again, the hook-up should be as close as possible to reduce the time lag. There was no opportunity to construct and test the bin described above.

(4) Slurry mixer. In the earlier tests using jordans as milling tools, the work was handicapped by the lack of an adequate slurry mixer and feeding device. It is also recalled that the tube mill feeding devices used at both Spence and Bakersfield mills were the source of much difficulty. It was believed possible to devise a unit which could deliver a thoroughly mixed slurry to any type of milling machine. Such a unit should not only be a suitable mill feeder, but also should permit accurate measurement and control of the

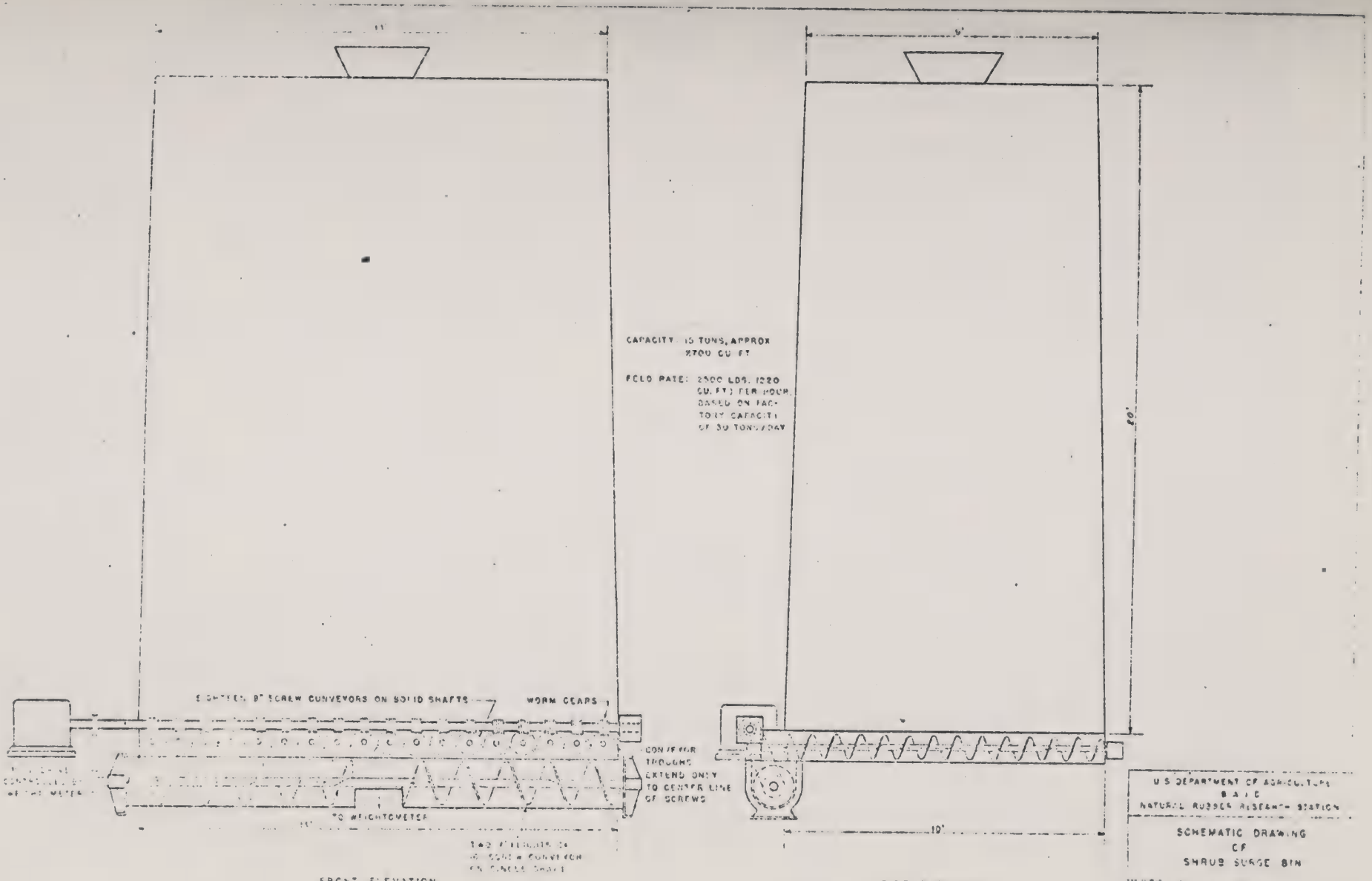

CAPACITY 15 TONS, APPROX
8700 CU FT
FEED RATE: 2500 LBS. 1220
CU. FT.) PER HOUR
BASED ON FACTORY CAPACITY
OF 30 TONS/DAY
WORM GEARS
CONVEYOR
TROUGHS
EXTEND ONLY
TO CENTER LINE
OF SCREWS
TO WEIGHTOMETER
FRONT ELEVATION
SIDE ELEVATION
10'
U S DEPARTMENT OF AGRICULTURE
B A I C
NATURAL RUBBER RESEARCH STATION
SCHEMATIC DRAWING
OF
SHRUB SURGE BIN

Figure 13

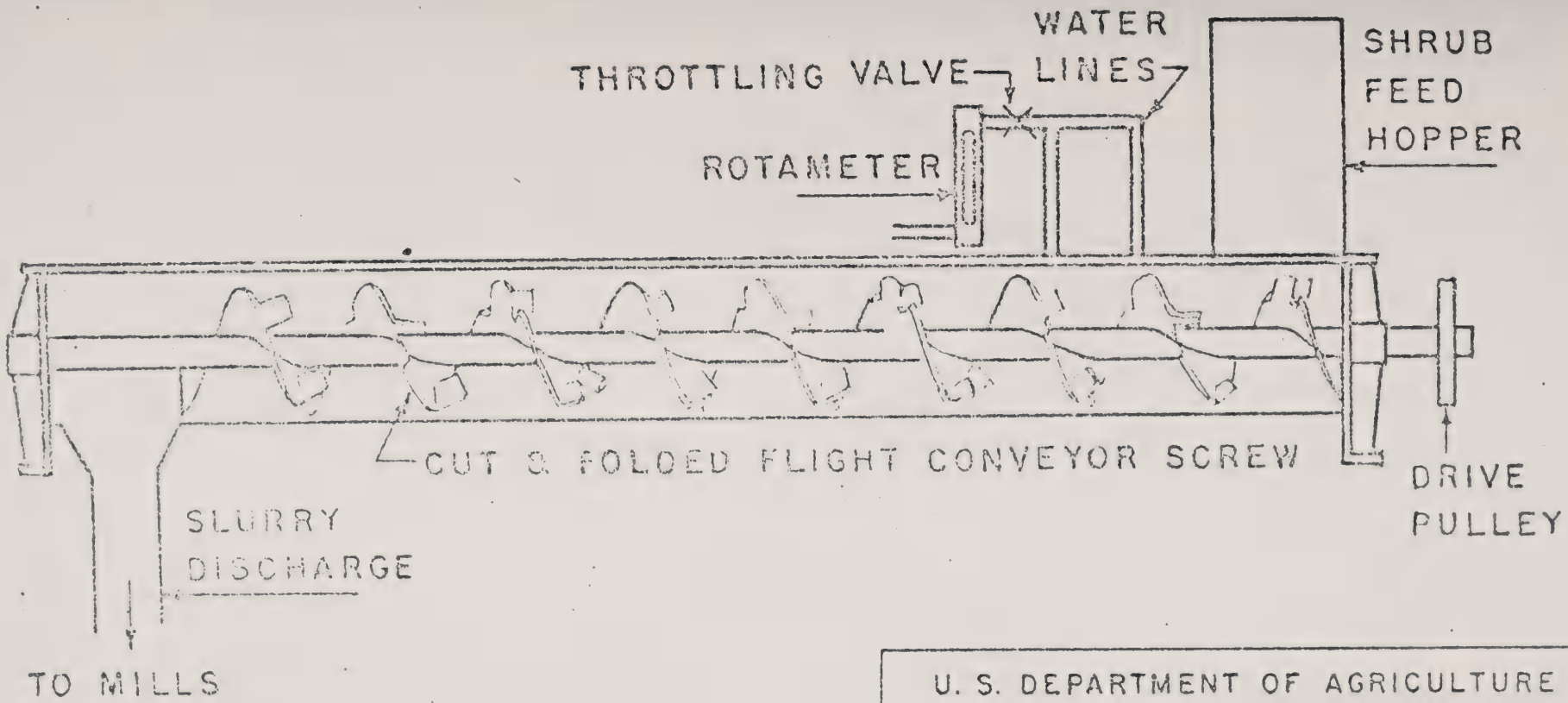
amount of water added to the shrub so that the desired water/solids ratios could be maintained. A feed device that met these requirements was designed and constructed. It is illustrated schematically in Figure 14. This unit was used only for the jordans, but with suitable modification would be applicable for other milling machines. Successful use of the slurry mixer is dependent upon the speed of rotation of the cut and folded flight conveyor screw. This speed should be fairly high in relation to the amount of material being fed, since it is necessary to keep the shrub material from dewatering before it enters the milling chamber.

(5) Rectangular flotation tank. During the Emergency Rubber Project, considerable work was done on the design and development of a rectangular primary flotation tank. During the progress of this development it was observed that at low rates of feed the coarser bagasse settled immediately at the point of entry into the tank; that the velocity of settling was fast enough at times to create a down current sufficient to carry rubber worms to the bottom of the tank where they were trapped by bagasse; and that for successful operation the horizontal velocity of entry over the lip of the feeder, as well as across the top of the tank, had to be in excess of 2 feet per second. When this condition was met the coarse bagasse settled gradually and there were no eddy currents causing rubber to be trapped.

A tank of this type was incorporated in the Bakersfield mill design. In operation, it was never entirely successful. This was partly due to the manner in which the feed was introduced to the tank. In addition, the bagasse was removed at intermittent intervals by an air lift. At these times, so much water was removed with the bagasse that the flow across the top of the tank was completely stopped. Down currents, caused by this excessive removal of water at the bottom of the tank, carried rubber out with the bagasse.

In the course of process research and development by the Natural Rubber Extraction and Processing Investigations Project, a new tank was designed and constructed. This tank was fitted with a constant level overflow, a drag conveyor, and a tubular screw conveyor for the removal of bagasse, and an improved slurry feed device. A schematic drawing of this installation is shown in Figure 15. In the early stages of use, the conveyor for removing the bagasse gave considerable difficulty by plugging up. When the speed of rotation of the screw was increased so that considerable water was removed along with the bagasse, no further difficulty was experienced. A high rate of flow across the top of the tank was maintained at all times. Under these conditions some fine bagasse was carried over to settle in the baica feed tank, but there was never any indication of floating rubber carried out with the bagasse.

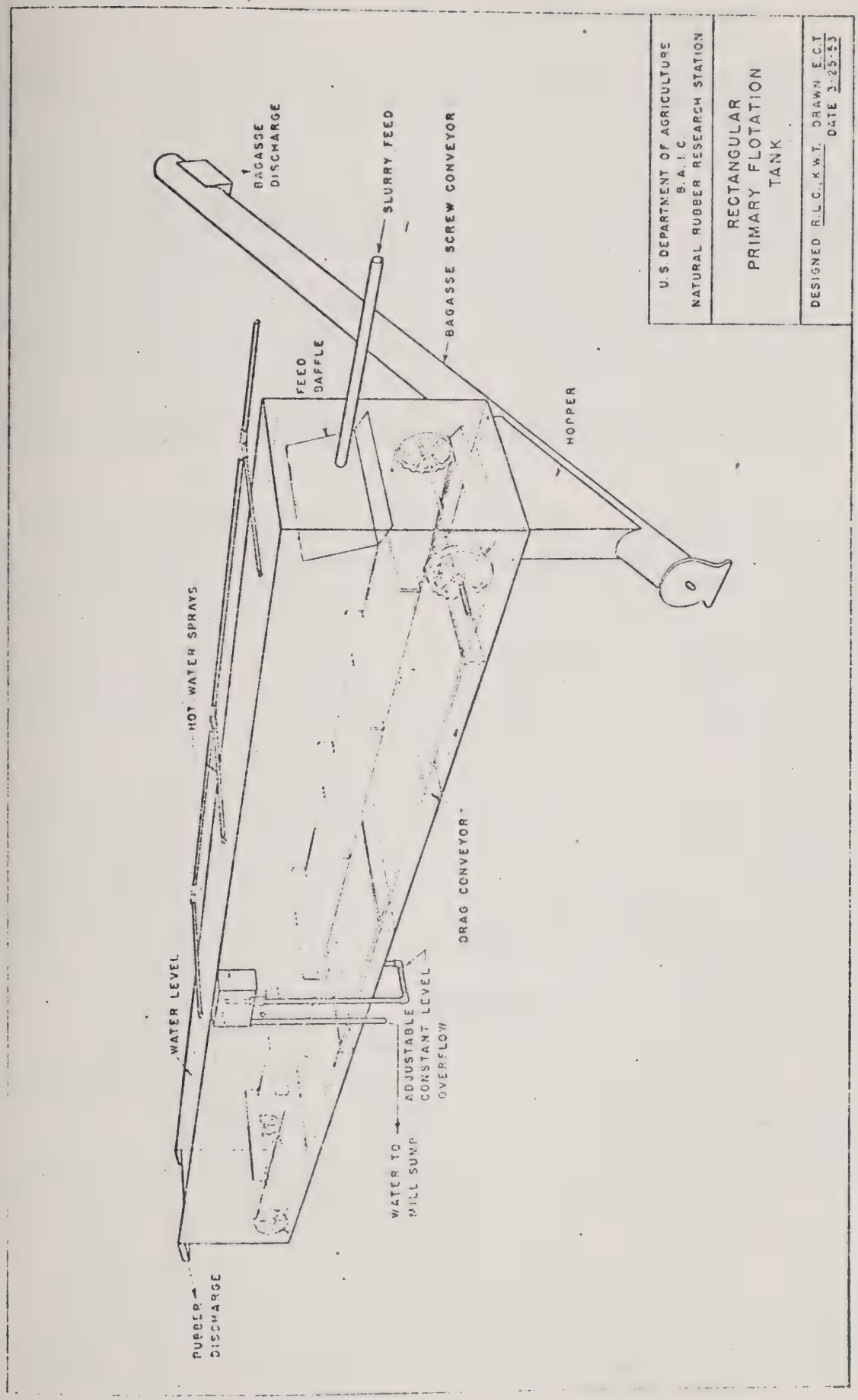
(6) Deresination equipment. The development work on a suitable type of deresination apparatus was carried out over an extended period of time. A thorough literature review indicated that almost all of the types of solvent extraction apparatus in general use were unsuited for the deresination of guayule as either shrub or rubber. However, it appeared that a continuous belt type of extractor for oleoginous substances might be suitable. To determine the feasibility of using such an apparatus, an extractor was built which consisted essentially of a segment of a belt in which the bed of rubber



U. S. DEPARTMENT OF AGRICULTURE
B. A. I. C
NATURAL RUBBER RESEARCH STATION

SCHEMATIC DRAWING
OF
SLURRY MIXER

DESIGNED K.W.T DRAWN E.C.T. 3-9-53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B. A. I. C.
NATURAL RUBBER RESEARCH STATION
RECTANGULAR
PRIMARY FLOTATION
TANK
DESIGNED R.L.C., K.W.T. DRAWN E.C.T
DATE 3-25-53
BAGASSE DISCHARGE
SLURRY FEED
BAGASSE SCREW CONVEYOR
FEED BAFFLE
HOPPER
HOT WATER SPRAYS
DRAG CONVEYOR
WATER LEVEL
ADJUSTABLE CONSTANT LEVEL OVERFLOW
WATER TO MILL SUMP
RUBBER DISCHARGE

Figure 15

remained static while the miscellae were moved countercurrent to it. This extractor and its use have been discussed under the "Deresination" section of this report.

From the data acquired from work done with this extractor, design drawings for a continuous belt extractor were made and supplies and materials for its construction were ordered. The necessity for producing rather large amounts of deresinated rubber for aircraft tire evaluation, coupled with slow deliveries of materials, precluded the building of this extractor. The original design called for the construction of an extractor in which extraction and drying would be carried out on a single belt. However, while preparing the rubber for aircraft tire manufacture, it was observed that after deresination the bed of worms became somewhat impervious to the easy flow of air that would be necessary in the drying operation. A schematic drawing of a revised two-belt, continuous, countercurrent extractor and drier is shown in Figure 16.

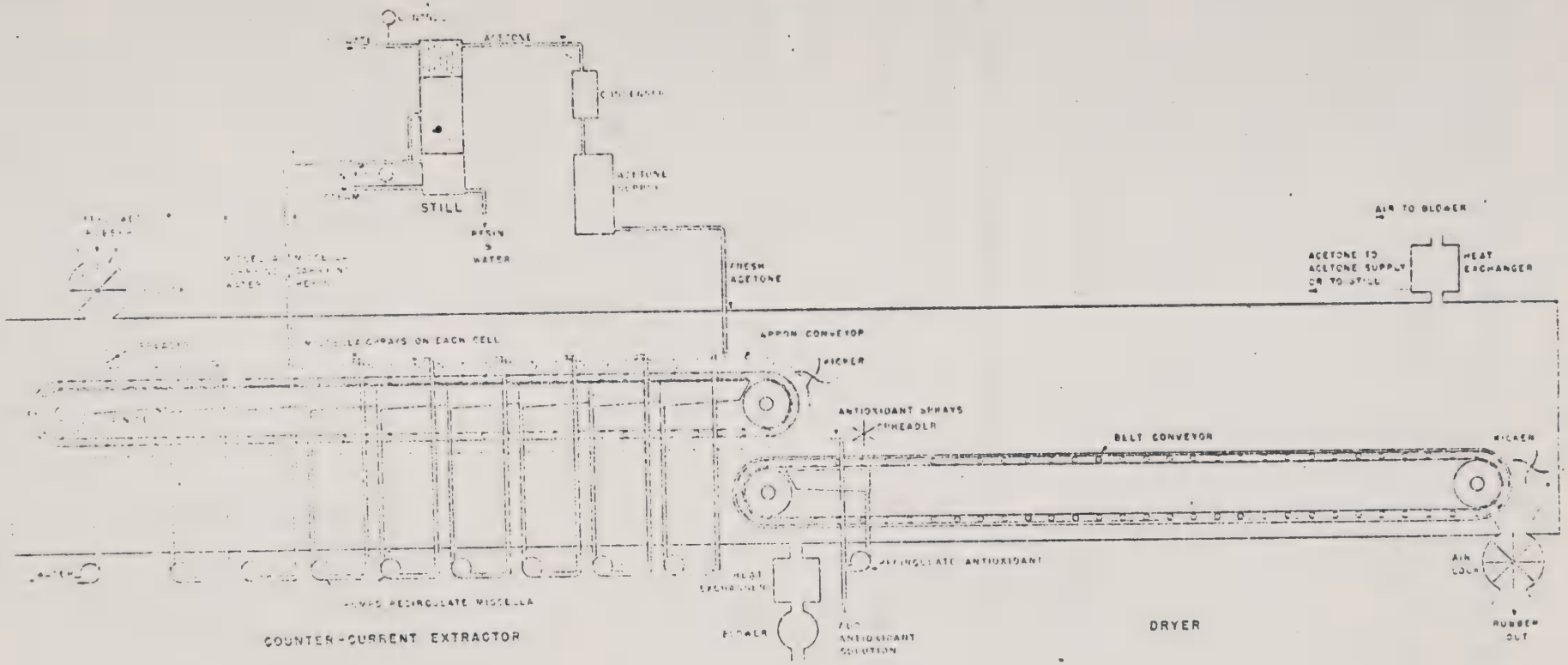
As now visualized, rubber from the discharge of the scrub mill flotation tank would be forced under a water seal or through another type of air-lock device and discharged directly onto a moving perforated belt. The rubber on the belt would be spread and leveled to an even bed by a kicker and doctor blade.

The space between the forward and return flights of the extractor belt would be divided into approximately 25 sections, each of which would constitute a receiving tank for the miscella passing through the bed of worms. Each of these tanks or stages would be equipped with a pump for moving the miscella.

The first section would serve merely as a drain section for the removal of the free water carried into the system with the rubber. The pump for that section would pump the water, coming over with the rubber from the scrub mill tank, together with any fines passing over, back to that tank. The other pumps would each pump to sprays above the belt so that miscella percolating through the bed would be returned to its own cell. The receiving tanks or stages would be so arranged and inter-connected that as fresh acetone was fed into the last stage, the quantity of miscella in the receiving tank would increase until the surplus would flow by gravity to the stage immediately preceding it - and so on back through the system. Miscella would be removed at stage No. 2 and at the stage of peak resin concentration in amounts equal in quantity with the resin and water entering with the rubber.

At the end of deresination, rubber on the belt would be broken up and spread on a second belt through which warm air would be circulated to remove the acetone. This air would be cooled to condense most of the acetone for recovery. The air would then be re-heated and recirculated. The dried rubber would then be discharged through an air-lock to be packaged for shipment to the consumer.

(7) Other machine development. Certain other machine design and development problems were worked out in the pilot plant. This work was essential to the carrying out of pilot plant research, and to the preparation of sufficiently large quantities of rubber for industrial evaluation. It did not,



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COMBINATION
COUNTER-CURRENT EXTRACTOR
& RUBBER DRYER

Figure 16

however, contribute to the development of facilities which would be included in a commercial factory. Brief mention may be made of such things as shrub conveying systems; a baica charging tank; a self-skimming scrub mill tank; devices for charging a batch-type scrub mill; a prepared shrub feeding device; a sample divider (previously discussed); and many other facilitating machines and equipment.

h. Byproduct Possibilities. This line of investigation was discontinued in July 1949 and, accordingly, received no direct attention since that time. However, in the course of subsequent processing investigations, including resin characterization studies, additional information germane to byproduct utilization has developed indirectly. Therefore, this section will consist of a survey of past developments expanded somewhat on the basis of the recent findings of related continuing projects. The byproducts of guayule which may be considered to have possible values are outlined, together with several projected uses, in Table 18.

Table 18. Potential Byproducts from Guayule

Processed Shrub - (Less the rubber)				
CORK	WATER SOLUBLES	RESIN	BAGASSE	LEAVES
(1-3%)	(10-12%)	(5-7%)	(50-55%)	(15-20%)
Linoleum filler	Irrigation Fermentable sugars (inulin) Pharmaceuticals (betaine) Inorganic salts	(See resin flow sheet) Drying oils (linoleic acid) Pharmaceuticals (parthenioi) Lube oil addends (terpenes) Carnauba substitute (wax)	Fuel Compost Pressed logs Pressed boards	Compost & fertilizer Chlorophyll Cutical wax

(1) Resins. Of the possible byproduct constituents of guayule, the resins appear to offer the most promise from the standpoint of financial return in connection with the production of deresinated rubber; and it has been this material to which practically all of the work under this project has been directed thus far. For variety 593, roughly one-half pound of resin is potentially available as a byproduct for every pound of rubber produced. Resin availability would vary with the variation of resin content of different strains of guayule. Essentially all of this resin could be obtained by solvent extraction of the shrub before milling out the rubber. Deresination of ordinary resinous rubber yields only about half the amount of resin that was present in the whole shrub. As pointed out in greater detail in the section on resin characterization, the resin differs also with respect to percentage composition of principal components - depending on whether it is essentially a total extractive as with "shrub resin", or a partial extractive as with "worm resin". Therefore, byproduct application of resin constituents would be dependent on the source from which the resin becomes available.

Recent investigations here have shown that upwards of 37 percent of the "worm resin" consists of unsaturated long-chain fatty acids, notably linoleic acid, along with traces of linolenic and oleic acids. Originally combined in the resin in the form of esters, these acids may be released by an appropriate saponification process (disclosed in patent application), and after subsequent clean-up steps be obtained as a marketable drying acid fraction. These acids may be obtained in varying degrees of purification and fractionation (see section on resin characterization), depending on projected end uses of the products obtained. Linoleic acid itself has long enjoyed an established position in the paint and varnish industry.

Cinnamic acid, present in resin as the ester of parthenol from which it may be obtained by saponification, is also a byproduct of established value in the cosmetics and pharmaceuticals industries. A recent wholesale price (Chem. & Eng. News, 31, 483 (1953) in 100-pound lots was given at $1.70 - $1.80 per pound.

A "drying resin" fraction (see section on resin characterization) readily obtainable from shrub resin by solvent manipulations is a hexane-insoluble, alcohol-soluble "shellac-like" gum resin which can be easily polymerized to a heat resistant clear coating of good solvent resistance. It is this fraction, constituting about 35 to 50 percent of the shrub resin, but a much smaller proportion of worm resin, which undoubtedly has been the portion of guayule resin of prime interest to varnish and paint manufacturers.

The terpenes of guayule constitute a potentially valuable "naval stores" type of byproduct. Volatile terpenes which comprise only about 3 - 5 percent of the worm resin, but a much higher proportion of leaf resin, include alpha-pinene, dipentene, cadinene, parthenol, and others. Sesqui-, di-, and higher terpenes are also readily obtainable in significant quantities from the non-volatile unsaponifiable fraction. Since additional characterization studies should be carried out on this fraction, it is not feasible at present to assess its future byproduct potential. However, several years ago one of the leading pharmaceutical companies (Armour) for a time considered using guayule-derived parthenol as an organic chemical intermediate in one of their processes (undisclosed, but possibly one of the synthetic adrenocorticotropic hormones). Their interest naturally waned when a regular supply of parthenol could not be guaranteed. The byproduct uses of the simpler terpenes, such as alpha-pinene, are well known and too numerous to cite here.

Future interest in parthenyl cinnamate and its saponification products are perhaps enhanced by the recent disclosure (U.S. Patent 2,572,046) of a novel process for its isolation from guayule resin by a liquid-liquid extraction.

Another constituent of guayule resins and/or water extracts of guayule shrub is betaine. Commonly obtained as a byproduct of the sugar beet industry, betaine has a limited market as a pharmaceutical and as an intermediate in the production of surface-active agents, disinfectants and other chemicals. It is also produced synthetically by the Chemo Puro Manufacturing Company, Long Island City, N. Y. An improved procedure for the isolation of betaine from plant extracts has recently been developed here (U.S. Patent 2,549,763).

The cuticle wax from guayule (constitutes about 0.25% of lush weight of the foliage) has always been regarded here as one of the most promising by-products of guayule processing operation. Its relative hardness, molecular weight, and melting point justify its consideration as a carnauba substitute or extender. In the present program, it has not been possible to devote much time to its separate investigation.

(2) Water solubles. The water solubles of guayule can be classified into three types, polysaccharides, amino acids, and inorganic salts. The polysaccharides comprise levulins (fructose polymers) and pentosans, including possibly xylan. The amino acids include betaine, discussed above. The inorganic salts have not been thoroughly investigated, but appear to include some oxalates and various potassium, sodium, and calcium salts. Of all these substances, the inulin-derived levulins are probably of greatest practical interest because of the possibility of their conversion to low cost alcohol. Present in the defoliated shrub to the extent of 8 - 12 percent (MFB), the levulins are readily extracted by hot water (80°C.). Thus, they will concentrate in the milling and other processing waters to the extent of 3 - 5 percent. Further concentration might result from greater re-use of process waters. The direct conversion of the high polymeric inulin to alcohol in 90% yield can result from fermentation with the proper strain of Saccharomyces fragilis (NRRL). Despite the high concentration of pentosans (xylan) in the guayule tissue (12-15%) its low solubility in hot water precludes the presence of much of this material in processing waters. If readily obtainable in significant quantity, it could be used as source material in the production of furfural. The processing waters have in the past also been used for irrigation purposes with no apparent harmful result on shrub growth. In such a case, the amino acids present might supply some of the nitrogen requirement.

(3) Bagasse. The bagasse constitutes the largest and probably least valuable byproduct, at least on a weight basis. Nevertheless, its importance as a source of fuel for guayule processing is indisputable. Work conducted at the time of the Emergency Rubber Project showed that properly dried bagasse can be made to supply all heat requirements needed for large processing operations. For this purpose bagasse must be dried down to 35 percent moisture content. This can be accomplished in two stages; first, a reduction to 63-65% moisture in a centrifugal filter, followed by further drying by means of stack gases. The entire operation, including the stoking, can be handled mechanically. Other uses suggested for bagasse include filler for brick, pressed logs, pressed board, and compost. When used as compost, considerable nitrogenous material must be added as the bagasse alone ties up the available nitrogen in the soil.

(4) Leaves. The leaves represent an important, albeit untapped, source of guayule resin, especially volatile terpenes, wax, and plant pigments. If parboiling and defoliation were necessary in the processing of guayule for rubber, as now seems probable, much of the value of the leaves as a source of resin would be dissipated. Leaves, however, do constitute an excellent soil amendment, particularly when composted. Leaves, after parboiling, can also be compressed into a sort of building board that, due to the structure of the leaves, possesses a pleasing pattern. As a source of livestock feed, leaves appear to have no value because of their unpalatability.

(5) Cork. The cork is conveniently obtained in a waterlogged condition from the baica discharge tank. Its finely divided form suggests use as a linoleum filler; however, it has not been tested for this purpose.

i. Factory Recommendations. At this stage of process research and development, it seems desirable by way of summarizing the work to date, to set forth all possible recommendations as to the features which should be incorporated in the design of a factory or mill for the production of raw rubber from guayule. It is recognized that the type of rubber to be produced, i.e., resinous or deresinated rubber, would govern certain phases of factory design and construction. It is assumed here that deresinated rubber only will be produced. This assumption is based on the demonstrated superiority of deresinated guayule over the resinous kind.

Attention is drawn that unequivocal recommendations cannot be made in many instances. Additional research is needed to demonstrate beyond reasonable doubt which type of equipment or which mode of operation should be employed. In some cases a method for accomplishing a given end has been developed, but process development is yet to be carried out. These matters will be treated more fully in the section "Recommendations for Future Research".

(1) Process line. Factory recommendations can probably be discussed most easily by employing a flow chart which illustrates the various steps. Such a flow chart is shown in Figure 17. The heavy solid flow lines illustrate process methods or those methods whose use has been subject to conventional acceptance, but whose actual superiority remain to be demonstrated.

The flow chart is largely self-explanatory, and all the discussion needed is a stepwise recapitulation of the process which would be recommended for a commercial enterprise. This follows:

1. Guayule shrub would be undercut in the field, lifted, baled, and transported to the mill without any field curing and with minimum delay.

2. The bales would be broken, parboiled in a continuous, automatically controlled parboiler, and the shrub defoliated in a rotary screened trommel.

3. Initial comminution of the parboiled shrub would be done in a forced-feed hammermill of the hay grinder type.

4. Shrub from the hammermill would be passed through crushing rolls that operated at differential speeds.

5. An automatically discharging bin would receive the shrub from the crusher.

6. Shrub from the surge bin would be automatically weighed and mixed with the proper amount of water.

7. The water/shrub slurry would be introduced to the first of a number of tube pebble mills operating in series.

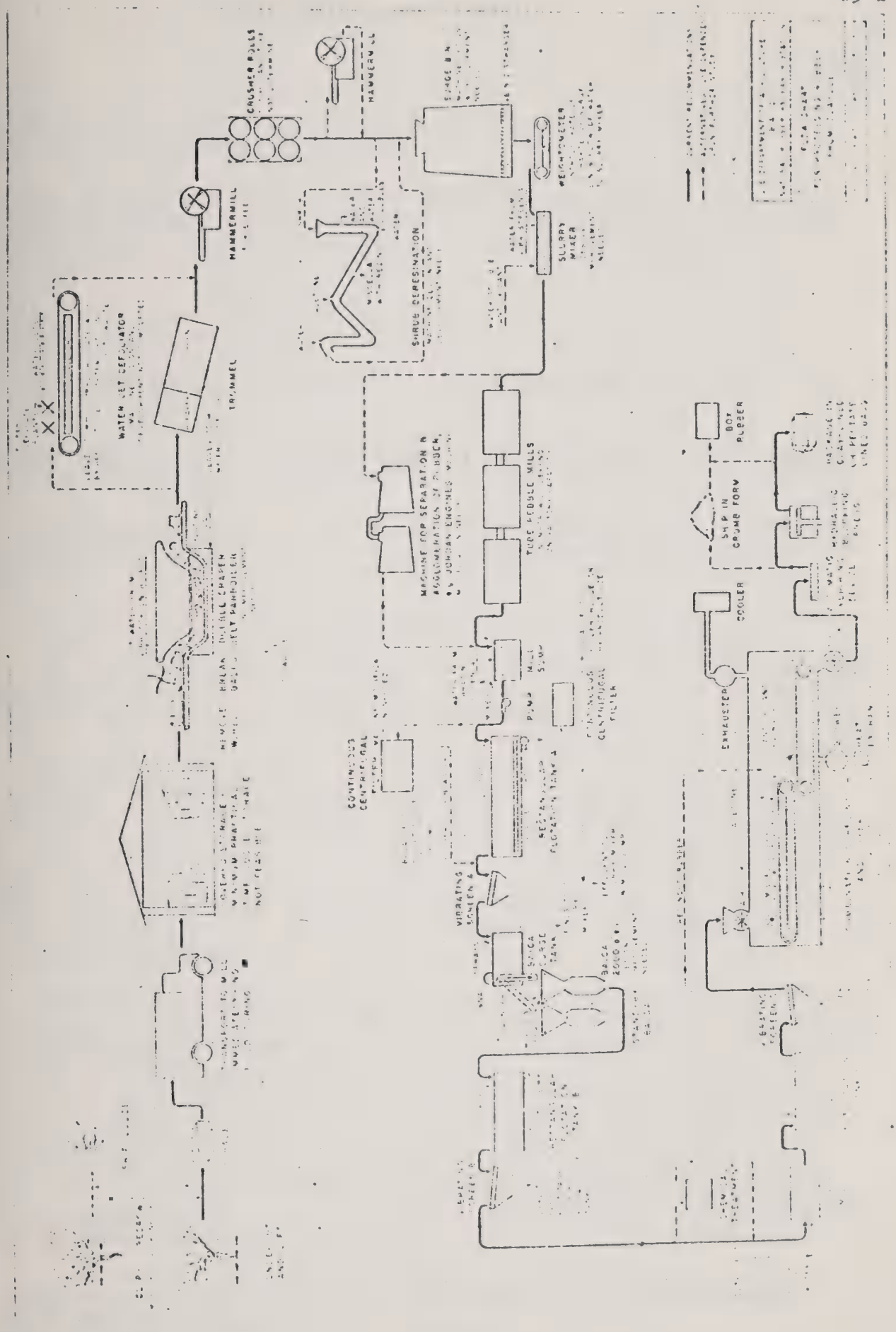
CRUSHER ROLLS
HAMMERMILL
HAMMERMILL
WATER JET DEFLOCKATOR
TRIMMEL
SHRUB DEFIBRINATION
SLURRY MIXER
TUBE PEBBLE MILLS
MACHINE FOR SEPARATION & AGGLOMERATION OF RUBBER
BOX RUBBER
SHIP IN CRUMB FORM
COOLER
ENNEUSTER
CONTINUOUS CENTRIFUGAL
CONTINUOUS CENTRIFUGAL FILTER
VIBRATING SCREEN
BARGA 2000 B.T.

Figure 17

8. Slurry from the last tube mill would be diluted with water and moved to a rectangular flotation tank.

9. The rubber and cork from the flotation tank would be dewatered and transferred to a baica surge tank. The bagasse from the bottom of the tank would be dewatered and dried for use as boiler fuel or for byproduct utilization.

10. Decorking would be carried out in a short cycle intermittent process under high pressure of about 2000 p.s.i.

11. After decorking, the rubber would be dewatered and given a scrub milling treatment.

12. From the scrub mill, the rubber would be floated in a rectangular tank then charged to a combination countercurrent resin extractor and drier.

13. In the extractor-drier, resins would be reduced to 2% or less on a dry, deresinated weight basis, a suitable antioxidant would be applied, and the moisture reduced to 1% or less on a dry deresinated basis.

14. After drying, the rubber would be packed for shipment.

(2) Water utilization. The guayule shrub thrives best under semi-arid conditions. Consequently the water requirements of a mill located close to the source of shrub supply is of vital importance.

Considerable study has been given to the amount of these requirements and the possible re-use of water throughout the process. While time and pilot plant facilities were not available for a complete investigation of this problem, enough work was done to justify the use of the following figures as a basis of calculation in the design of a future mill. These figures (Table 19) are based on the requirements of 100 pounds dry weight of parboiled and defoliated lush shrub with a 15% rubber content. The crude resinous rubber produced from that amount of shrub would make one charge for the baica which was in use during the life of this project.

These figures represent only the water moved from one piece of apparatus to another. The water added to the shrub to make a mill slurry with a 5 to 1 water-to-solids ratio, and that used to dilute this slurry after being milled to a 40 to 1 ratio for pumping over the primary flotation tank is water from the primary flotation tank. It consists of water separated from the bagasse after its removal from the flotation tank and water separated from the rubber floated over the vibrating screen, plus any water that might come from a constant level overflow. The 93 pounds required for make-up would be added as sprays on the primary flotation tank 7/. The 173 pounds used on the baica would be divided about as follows: (a) a major portion would be used to maintain the level in the baica feed tank and would be applied intermittently as

7/ Some provision should probably be made for cooling the water used in making the mill slurry.

Table 19. Projected Water Requirements for Processing Guayule Shrub

Apparatus	Water in with material		Water out with material		Loss or make-up required	Make-up Source
	Pounds		Pounds		Pounds	
Parboiler and shrub preparation	Shrub	85	Shrub	67		
			Leaves	58	80	Baica flotation tank
			Evaporation	40		
Mill and primary flotation	Shrub	67	Bagasse	120		
			Rubber	40	93	Baica flotation tank
Baica and baica flotation	Rubber	40	Rubber	40	173	Scrub mill
	Make-up baica charge	145	Water	173		Flotation tank
	Rinse baica	28				
Scrub mill and flotation tank	Rubber	40	Rubber	40	187	Recirculated
	Dilution water	360	Dilution	360	173	Fresh hot water

a spray to move the rubber into the snail while it was operating; (b) a small portion would be used to rinse the feed hopper and make up the baica charge; and (c) the remainder would be used to rinse out the baica after it discharged.

The 187 pounds of water recirculated for scrub mill dilution would come from under the screen separating out the rubber from the scrub mill flotation tank discharge.

The amount of fresh water required, as cited above, does not take into account the water required for boiler make-up or for other minor services around the plant. The fresh water required amounts to 170 to 200 pounds, or 1.7 to 2 pounds per pound of shrub.

While these figures represent the minimum requirements, they are not necessarily optimum. However, the work done with the jordans using recirculated water for making up the mill slurry would indicate that they are also the optimum.

D. Recommendations for Future Research

A perusal of the foregoing report on Process Research and Development reveals only too clearly that research in this field is a long way from completion. In the summary "Recommendations for Factory Desiga", certain steps in the process or the use of given types of equipment have been advocated solely on the basis that they have gained conventional acceptance over a long period of trial and error experimentation. It is the purpose of this section of the report to set forth specific recommendations as to the elements of research which must be resolved before the most practical in factory design and construction can be delineated.

1. Harvest Methods

Virtually no basic work has been done on the whole problem of harvesting. It has been demonstrated that it is necessary to process guayule within as short a time as is feasible after the plants are harvested. Probably the first problem to be solved is the manner in which the harvest is to be carried out. There are two approaches to the problem. In one the plants, after reaching a suitable age, may be undercut and completely removed from the field. In the other the plants may be pollarded, that is, the aerial portions may be cut off and removed for processing - leaving the root systems in the ground for re-establishment of the stand by regrowth and ultimate reharvest. Research on the manner of harvest will have to consider the physiological ability of the plants to withstand pollarding at various times of the year and under varying climatic conditions. It will be necessary to determine how many times the plants can be pollarded before stand renewal with new planting stock is necessary. And in the final analysis, an economic study of pollarding as compared to undercutting will have to be made. Decision as to the manner in which the shrub is harvested will be, in part, dependent upon the processing techniques to be used.

When a decision is reached as to the manner in which the harvest is to be carried out, it will be necessary to develop machinery appropriate to the harvest method employed.

Handling the shrub after it is harvested also poses problems. It has been advocated that the shrub after harvesting (either by pollarding or undercutting) be cut into fairly short lengths by some device such as an ensilage cutter, after which it would be elevated into a conveyance to the factory for processing. This method of handling presents certain drawbacks in that shrub so treated would be difficult to parboil and defoliate. Baling either whole or pollarded shrub could be more advantageously handled than could cut shrub. Regardless of the method employed, suitable machinery will have to be developed.

For both harvesting the shrub and handling it in the field after harvest, it is believed that machine development would consist primarily in strengthening and perhaps slightly modifying digging, cutting, and baling equipment presently available for handling other farm crops.

2. Parboiling and Defoliation

Parboiling, followed by defoliation, has been an accepted practice for the demonstrable reason and for several reasons that are supported by logic, but for which tangible evidence is lacking. Leaf material constitutes approximately 25 percent of the dry weight of the plants, and obviously constitutes a non-productive load on the milling system since the leaves contain no recoverable rubber.

There are other reasons for treating the shrub with boiling water before introducing it to the mill circuit. It is known, for instance, that boiling shrub induces coagulation of latex within the cells. However, additional research is needed to establish the length of time required to reach the maximum practical amount of coagulation. Correlative to this investigation, a study should be made upon the effect of variations of time of parboiling on the character of the rubber as reflected by its molecular weight and the cleanliness of the new rubber. There is some evidence which indicates that milling the shrub without leaf removal increases the amount of metals, especially copper, iron, and manganese, in the raw rubber. These metals in particular are deleterious to the keeping quality of the rubber, and investigations should be made to determine the effect of the presence of leaves in the mill circuit on rubber quality.

In the event that parboiling and defoliation are essential to the recovery of high quality rubber, then utilization of the leaves as a by-product must be studied. It is known that leaves possess some advantageous properties as an agricultural fertilizer. They are also a source of resinous material and might prove to be of value for their chemical products. Again, they might be compressed into a satisfactory structural material.

Equipment for parboiling and defoliation has been partially developed. A revised form of continuous parboiler for handling loose plants or broken bales has been designed. Such a unit should be constructed and tested. If

the plants are to be pollarded this means they will be received as a mass of individual branches. It may be that parboilers designed thus far will not handle this type of material satisfactorily. It is suggested that it may be necessary to include a bottom draper belt as a necessary part of the parboiler design, regardless of the type of shrub fed to it.

A rotary trommel has been suitable for defoliating the plants after parboiling, except in the case of pollarded shrub. During the Emergency Rubber Project one field was harvested by pollarding. In this case, the loss of twigs and branches through the screened section of the trommel approximated 30 percent of the original dry weight. Some other form of defoliator would have to be developed if pollarding became the standard harvest practice. It will also be necessary in this, as well as in other process steps, for processing research to keep abreast of the developments in the field of plant breeding. Some of the guayule x stramonium hybrids have very large leaves. A trommel equipped with a screen large enough to pass these leaves would, most likely, result in excessively high losses of branches and twigs. Additional machine design and development might be necessary to cope with this problem.

3. Shrub Comminution

No additional research is needed on the original comminution of the shrub of existing varieties. As previously pointed out, conventional force-feed hay grinding hammermills are available for this. It might be necessary to strengthen certain parts of commercially available grinders to render them suitable for handling guayule. It is possible that hybridization might result in the development of strains which would require a different form of original comminution apparatus. Even in this event, it is believed commercial equipment could be found which would be suitable even if it were necessary to utilize a machine such as a "hog".

Crushing presents quite a different problem. All of the work carried out by the Natural Rubber Extraction and Processing Investigations Project was done with one type of crushing rolls which were equipped with rather deep grooves and narrow bands. It is known that secondary and tertiary crushing can be done more advantageously if the rolls having relatively shallow grooves and wide bands are employed. Additional research is needed to establish the pattern of roll surface which would bring about maximum rubber recovery and to establish how many sets of crushing rolls would be required. Work should also be carried out to determine whether a hammermill or other form of disintegrator following crushing would be required or would eliminate the need for any or all crushing rolls.

4. Mill Circuit Feed

The work required here is primarily machine design and development. A preliminary design for an automatically discharging bin has been prepared. Structural design drawings should be made and a bin constructed which would be large enough to demonstrate its practicality in a mill circuit. A method of preparing a slurry by the intimate mixture of water and shrub has been developed. The slurry mixer is, of course, subject to improvement. It might

be advisable to put a pump ahead of the rotameter in order to maintain a constant pressure to avoid fluctuation in the amount of make-up water.

5. Milling

Probably it is in this field that the most work in process research is required. Although little work has been done on yields from tube mills and jordans, it probably represents the most accurate work done in this field 8/. In these limited trials, the paper-making jordan apparently resulted in a higher percentage-wise recovery of rubber hydrocarbon than did the tube mills. The tube mills have been included in the factory recommendations of this report because they have received commercial acceptance and because more work with the jordans needs to be done.

Additional work should be carried out using the tube mills as milling tools. In the work done by the Natural Rubber Extraction and Processing Investigations Project, it was difficult to maintain the desired water-to-solids ratio over any extended period of time. Frequently it was necessary to add water between the first and second mills to prevent the slurry from plugging up at this point. Water-to-solids ratios could probably be maintained more accurately by installing a pump in the supply line ahead of the rotameter so that the pressure would remain constant. Some mechanical device should be used between mills operated in series so that it would not be necessary to force the slurry from one mill to the next with water. It is conceivable, too, that the feed rates used were too high so that maximum yields from the tube mills was never achieved. All these factors should receive additional investigation. There is one point, however, which should not be overlooked by the future researcher. A certain amount of by-passing is bound to occur in a tube mill, and this in turn will result in under-milling of a part of the plant material with resultant low yields. This by-passing effect could be studied by dyeing a large mass of shrub and feeding it into the mill circuit during a long run. Microscopic examination of the slurry would then provide information as to the extent of by-passing.

Investigations with tube mills should also encompass variation in mill speeds, and with ball mills of other types such as the Hardinge conical ball mill.

Additional work should be carried out with jordans. All work carried out to date has been done with conventional paper-making equipment. It is suggested that jordans equipped with wider bars and thicker woods, so that the channels between bars are shallower, might result in higher rubber hydrocarbon recovery. The field for variation and improvement in the jordans is large indeed, and should be exploited to the fullest.

In addition to jordans, there may be other types of equipment suitable for separation of the rubber from the plant material and its aggregation into

8/ It should be remembered that all data obtained in these tests resulted from the "shaker method" of shrub and bagasse analysis and, hence, are more accurate than the yield data presented in the batch mill studies.

recoverable particles. More and more the feeling has developed that the successful recovery of rubber lies in a release of rubber from the plant cells in the shrub preparation steps, and that what has been termed milling in the past is, in reality, actually a matter of agglomeration of the already released rubber into a form that can be recovered by flotation.

In addition to the milling research indicated in the preceding paragraphs, research in this field will also have to take into consideration the development of new varieties and hybrids. These might pose problems which have not been encountered so far.

6. Flotation

Aside from redesign and construction of an improved rectangular flotation tank, very little work on flotation was done. Originally it was planned to do considerable work with a continuous centrifugal filter (Bird Machine Co.). The unit bought for this purpose was purchased in accordance with two rather widely divergent specifications. On the one hand the machine was to be used as a clarifying device in the recovery of rubber as latex; on the other, it was to be used as a means of recovering solid rubber from either jordan or tube milling. The internal structure of this machine was such that every time it was used for the recovery of solid rubber the effluent discharge passages plugged. Research on the use of such a flotation mechanism is strongly advocated because it appears that such a device would be required for dewatering the bagasse in any event, and if it could also be used as a flotation mechanism, the rectangular tank with its auxiliary equipment would be eliminated in a factory.

During the Emergency Rubber Project, a continuous centrifugal of the same make, but of somewhat different internal construction, was investigated by the Bureau of Agricultural and Industrial Chemistry as a mechanism for flotation. In a great many trials there are no recorded instances of this machine having plugged with rubber at the effluent discharge. Therefore, there is considerable reason to believe that such a filter could be used for flotation if the counter balances and surfaces of the solids removal screw, especially at the effluent discharge end, were streamlined and smooth; and if the effluent discharge ports themselves were modified to offer less impedance to the passage of the rubber worms.

7. Decorking

The method of decorking, that is, decorking under a high hydraulic pressure, short cycle treatment, has been proven. A machine for this purpose, a "baica" had been designed by the BAIC under the Emergency Rubber Project. Preliminary tests were made at that time. It had a design capacity of 21 gallons and was supposed to handle approximately 1 pound dry raw rubber per gallon of water. It has since been used under conditions that simulated factory operations. This use revealed certain shortcomings which should be corrected in a prototype design. These are enumerated and corrections suggested as follows:

a. Baica Charging Tank. A certain amount of plant material is carried over from the primary flotation tank due to the high velocity maintained

across the top of that tank to prevent sinking rubber. No provision was made for removal of this material. It could probably be accomplished by the use of a screw conveyor as shown for the primary flotation tank.

b. Metering and Dumping Bucket. The baica as presently designed is equipped with a metering bucket which serves to measure the amount of material required for a single baica charge. The material is metered by having an overflow which allows the excess rubber, cork, and water to drain to the slurry sump from which it is moved to the primary flotation tank for ultimate recovery. At the proper point in the baica cycle sequence, the metering bucket tips to discharge its contents into the baica charging hopper. No provision was feasible for rinsing out the metering bucket, with the result that a certain amount of rubber adhered to the inside walls. Eventually this clinging material would choke up the discharge spout of the bucket and interfere with its efficient functioning. Also the adhering rubber would become degraded and slough off into the baica, with the result that the end product would be contaminated with degraded material.

Two possible methods for correcting this condition are suggested. First, it seems possible that the baica charging hopper itself could be made to serve the dual purpose of metering bucket and charging hopper. Under the present operating system, the baica is discharged by first opening the bottom valve and, after a few seconds delay, opening the top valve. It might be possible to empty the baica completely without opening the top valve during the discharge. This would permit elimination of the metering bucket as a separate entity. It is recognized that this manner of operation would extend the time of the baica operating cycle. Second, if the baica could not be operated successfully by opening the bottom valve only, then the metering bucket should be mounted in a stationary fashion directly over the charging hopper. This would eliminate the need for tipping the bucket and consequently the need for a discharge spout. It would also permit the use of powerful rinse sprays which could be so devised as to eliminate the accumulation of rubber.

c. Baica Charging. As noted above, the metering bucket delivers a normal charge to the baica. This charge does not fill the baica chamber completely. This is accomplished by the use of wash sprays located in the charging hopper which not only are supposed to finish filling the baica chamber, but which also wash down rubber adhering to the hopper walls and wash off the top valve and valve seat so that valve closes. This action is supposed to insure proper seating of the top valve. The operation of these sprays is initiated by an automatic electric timer and terminated by a limit switch actuated by the top valve stem on the closing stroke. Adjustment of the timer to obtain just enough water has been difficult. If the metering bucket is short in its contents, then not enough water is added so that the system does not build up to pressure as is required. This situation can be corrected in another way as will be discussed below. On the other hand, frequently the sprays deliver too much water so that when the top valve closes there is water plus some cork and rubber in the charging hopper above the valve. The floating rubber and cork are discharged in the baica discharge phase without receiving any pressure treatment. It is suggested that the baica barrel could be fitted with some sort of float switch, or other limiting device, which would close a second valve controlling the sprays (or would

close the top valve) when the liquid level in the baica had reached the precisely correct point.

d. Hydraulic System. As presently designed and constructed, the hydraulic system is not adequate. Its capacity and length of stroke should be increased so that if the baica chamber is not quite full (as discussed above) pressure will be built up to the required 2000 p.s.i.g. by the reserve cylinder capacity. If the line pressure which actuates the hydraulic system is subject to any material variation, it will be necessary to install a pump in the line ahead of the low pressure cylinder to maintain a constant head of pressure. In work during the past five years it was found necessary to maintain this pressure at approximately 70 p.s.i.g. in order to insure satisfactory operation.

e. Controls. As the baica is now constructed, many of the sequential operations are governed by an automatic electric timer control. A redesign of the baica would do well to take into consideration the possibility of using limit switches which would be actuated mechanically by the movement of valve stems, float valves, lugs on roller chains, and similar devices. This would insure that no operation would succeed any other operation until the machine was ready for it. As an example of this and if a metering bucket were required, a limit switch could be installed so that opening the top valve would close the limit switch - which in turn would cause the metering bucket to discharge. Thus it would be impossible for a charge to be placed in the baica unless the top valve were open to receive it.

Refloating the rubber after the decorking treatment poses no particular problems except that provision for removal of cork from the bottom of the tank would have to be made.

8. Scrub Milling

Pebble mills, either tube or batch, have been used in conventional milling practice and in research. It seems probable that pebble mills will remain to be the best tool for this purpose. However, other types of equipment should be investigated to see if they could be used "as is" or after modification.

Perhaps one of the more fertile fields for investigation is the chemical treatment of the rubber before or during scrub milling. Treating the rubber with ammonium hydroxide holds some promise in reducing the amount of residual plant material in the crude. Use of other caustics such as sodium or calcium hydroxide is not favored because it has not been possible to inhibit their deleterious effects on aging characteristics. These effects are believed to be due to the residual metallic ions. Some of the modern detergents might be effective in reducing insolubles.

9. Deresination and Drying

Additional research on deresination will depend in part on the decision as to whether shrub is to be deresinated prior to milling, or whether wet rubber worms are to be deresinated after milling. The present view inclines

to the deresination of the wet rubber worms. Accordingly, only a few salient features of shrub deresination will be discussed.

A method of shrub deresination has already been successfully developed. Presumably, shrub could be deresinated in a belt type of extractor similar to that recommended for wet worm deresination. Provision would have to be made for backwashing the residual water out of the shrub after deresination was complete. It would not be necessary to dry the shrub before it was milled.

Drying the rubber milled from deresinated shrub would probably be done by the use of acetone to avoid the deleterious effects of high temperatures in drying. Equipment for this would have to be developed.

Turning now to the deresination of wet rubber worms, it may be said that the method for accomplishing this has developed to the point when continuous countercurrent equipment must be employed. However, many factors governing the design of such a machine still remain to be investigated. Some of these could be solved on the static bed extractor already developed, but by far the simpler now would be to construct a small model of a moving belt extractor as previously described. Original design drawings for a combined single belt extractor and drier have been made. In light of the most recent findings, however, this design should be altered to a two-belt unit in which the first belt would constitute the extractor section and the second, the drier section.

On such a model, some form of feed device would require development. An inverted siphon might be used if some way could be found to keep the water and rubber in intimate mixture until deposited on the extractor belt. Failing this, some form of air lock would have to be developed which would deposit rubber on the belt without an attendant escape of acetone-laden vapors. Some mechanism would have to be developed for spreading an even bed of rubber over the belt. Also needed is a type of non-clogging spray which would distribute the miscella uniformly over the entire bed of worms at a rate sufficient to flood the surface without disturbing the bed.

The ratio of openings to total area of the belt to preserve the correct balance between flooding and free penetration to all the worms needs to be studied. There is also need of a method of preventing the by-passing of miscella over the edges of the mat of rubber as it shrinks during deresination.

The conditions for optimum deresination in the apparatus already studied probably would not apply in full to a moving belt and would need further consideration. This applies particularly to the time the rubber is flooded, i.e., the spacing and number of the sprays, the amount of time, that is, the distance the belt moves, that would allow adequate drainage, as well as the ratio of area flooded to that required for proper drainage.

In the application of antioxidant, the chief problem would be the maintenance of proper concentrations of the antioxidant solution. As this would vary with the type of chemical used, no general rule could be applied.

Runs would have to be made under widely varying conditions to determine the effect of deresination on the rubber mat of worms produced at various

seasons of the year; from different strains of shrub; from different ages of shrub, etc. The effect of temperature, time of deresination, miscella concentration, etc., on each of the above factors would also have to be studied, before enough data would be available for a final design.

These studies would have particular interest in the problem of recovery of solvent from the deresinated rubber. For instance, if the bed becomes dense under the usual conditions of operation and does not allow free circulation of air to all parts, then it would have to be broken up and transferred to a second belt as has already been mentioned. If, on the other hand, it remains porous and allows free circulation, no transfer would be needed. If the bed could, in all cases, be easily broken up into discrete worms it might be possible - and perhaps more economical - to recover the solvent from the worms in a tower much as is done in spray drying.

10. Packaging

In the past it has been customary, in commercial scale operations, to package raw guayule rubber by placing two 100-pound bales in a wooden box. During the Emergency Rubber Project, some investigation was made as to the feasibility of packaging guayule in paper bags - either lined or unlined. The indications obtained in these investigations, and in the present limited studies, were that packaging in this manner would be feasible. In view of the increasing shortage of wood and the high cost of box shook, this line of investigation might profitably be pursued further.

11. Latex Research

Rubber in latex form serves a number of important uses such as for the manufacture of foam rubber, gloves, balloons, and other dipped goods for which solid rubber cannot be used as the raw material. In these and related applications guayule latex could undoubtedly be utilized - at least as a partial replacement for Hevea latex.

However, on the basis of the results obtained in the investigations conducted thus far, it does not appear that the development of a practicable and economical process of extraction is in favorable prospect. The line of investigation leading to complete process development of deresinated solid rubber, of quality equivalent to Hevea rubber in heavy-duty truck tires, which has shown marked progress since the abandonment of the latex investigations, appears to be far more worthy of continued effort.

Nevertheless, if requirements for natural rubber latex became critical under an emergency which would justify the continuance of efforts to produce guayule rubber latex, a number of difficult problems would need to be solved. Broadly, those problems which require further and extensive investigation include: (1) Development of practical means of complete disintegration of the latex-bearing cells for release of all of the rubber without coagulation of latex; (2) Development of means for recovery of the rubber which has been unavoidably coagulated within the shrub prior to processing for latex; (3) Development of economical and continuous procedures for separation of both coarse and colloidally suspended plant material from the initial latex

dispersion; (4) Centrifugal concentration or "creaming" of separated latex from approximately 1 - 2 percent dispersions to commercial products of about 60 percent; and finally, (5) Development of a complete latex extraction process through the pilot plant stage and translation to factory scale.

12. Byproducts

Process research and development on byproducts from guayule would consist primarily of machine design and development following basic laboratory work. Byproduct research would center on leaves, bagasse, resin, and possibly water solubles.

13. Economics

As an integral part of any process research program, cost studies must be carried out to determine the maximum economic feasibility. In large part these studies could and should be carried out concurrently with other phases of process research and development.

Of the items to be studied, and ones which can most easily be studied in connection with other phases of research, are those of power requirements. Each step should have power requirements established on a pilot plant scale in such a manner that they could be extrapolated to full scale factory operations. Power requirement studies will also have to be made on alternative machines before an intelligent selection can be made. An example of this may be found in milling equipment power. At the present stage of research, it appears that tube mills and jordans are about equal in their efficiency as rubber separation and agglomeration equipment, with the jordans possessing a slight edge. A power study might reveal that power demands for one machine would completely eliminate it from further consideration.

In conjunction with power requirements as such, a survey of fuel costs will be necessary. Analysis of these costs will be dependent upon the geographical area where it is expected a factory will be located. The costs and availability of different kinds of fuel such as coal, oil, and gas must be determined and these factors applied to a factory of given design and capacity. In this connection, it is well to note that guayule bagasse is an excellent fuel when properly handled. Reliance upon bagasse as a source of fuel will be more or less dependent upon a more remunerative use of bagasse as a byproduct.

In all the commercial guayule mills operated to date, labor costs have been inordinately high. Most of the excess labor is used in two phases of processing: in the shrub preparation department, and in packaging the rubber for shipment. In both instances it appears that labor requirements can be materially reduced through more complete mechanization of the various operational steps. Throughout the entire factory the utilization of automatic controlling and recording equipment should reduce labor requirements, and result in an end product of enhanced quality and uniformity.

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SECTION III

LABORATORY INVESTIGATIONS

Index

Index (Cont'd) Page

III. LABORATORY INVESTIGATIONS

A. Analytical Research and Development

The analytical section was organized for two purposes (1) to do routine chemical testing for the other research groups of the project and (2) to develop new methods and improve old methods so that they would be more useful, accurate, and precise. Existing methods were replaced with new and improved methods as they became available. During the 64 months the laboratory was operated, nearly 14,000 samples were analyzed for an average of three constituents in duplicate or triplicate. This was carried out with an average of two full-time analysts and part-time services of one scientific aide.

1. Methods Used by Emergency Rubber Project

Most of the methods in use during the Emergency Rubber Project were standard or had been developed at the Eastern Regional Research Laboratory just prior to the opening of the Salinas Laboratory. A few new methods were developed as the need arose. A modified triple solvent procedure was used to determine rubber hydrocarbon and resin in shrub, effluent, and bagasse. Rubber hydrocarbon in the crude rubber was determined by a modified bromination procedure. Trace metals were determined by spectrophotometric procedures.

The methods in use during the Emergency Rubber Project were the best available and little useful research could have been accomplished without them. However, they were time-consuming and did not have the desired accuracy. This was particularly true of the rubber hydrocarbon analyses. Pilot plant yields based on laboratory analyses of the original shrub, for example, sometimes exceeded 100% and total rubber accountability was frequently as high as 110%.

2. Current Methods and Their Application

The importance of accurate and precise analytical methods in process research and development cannot be over emphasized. Because of this fact, much time and effort has been expended in improving existing methods and developing new methods. Considerable success and some failures have attended these efforts. Although much remains to be done, it is fair to state that the current methods of analysis pertaining to guayule are more reliable and faster than the methods in vogue at the beginning of this project. Rubber yields in excess of 100% are no longer obtained and rubber accountability is rarely over 100%.

For the benefit of future researchers, the current methods of analysis and developments leading up to these methods are given here in considerable detail.

a. Rubber Hydrocarbon by Bromination. In the method described by Willits, Swain and Ogg, addition of bromine is accompanied by some substitution. The substitution portion of the bromination reaction is difficult to

control and has contributed to low results and occasional poor precision. Work was carried out to investigate the effect of several factors on the bromination reaction and to find a means of inhibiting the substitution reaction. It was found that the effect of rubber hydrocarbon concentration on bromination is critical. Iodine accelerates bromination but is not present in the final product. Temperature and light are important variables. The bromination reaction is insensitive to bromine concentration, so long as a considerable excess is present. Trichloroacetic acid in the amounts used to assist in the solution of raw rubber has no effect on the results. Addition of chloroform to the benzene solution of rubber inhibits the substitution reaction with no apparent effect on the addition reaction. Factors for converting rubber bromide $(C_5H_8Br_2)n$ to rubber hydrocarbon of 0.299 for Hevea and 0.300-0.301 for guayule were obtained. These agree well with the theoretical factor of 0.2988 for a completely additive product and are somewhat higher than the 0.292 reported by Willits et al. This work was published.

(1) Bromination procedure. Bring the rubber-benzene solution to the mark in a 250 ml. volumetric flask at 25°C. Pipet a 25 ml. aliquot at this temperature (containing 30 to 50 mg. of rubber hydrocarbon) into a 250 ml. beaker. Add 9 ml. of chloroform from a buret and 2.5 ml. of the brominating solution to the rubber solution. (The brominating solution is prepared by dissolving 2 grams of C.P. iodine in 10 ml. carbon tetrachloride, filtering and adding 5 ml. of C.P. bromine to the filtrate). Place the beaker in a water bath at 25°C. and allow bromination to proceed for 100 ± 5 minutes. No direct sunlight should come in contact with the solution in the water bath. At the end of the 100 minutes remove the beaker from the water bath and add approximately 200 ml. of 95% ethyl alcohol to the contents of the beaker. Allow two hours for the rubber bromide to settle.

(2) Determination of rubber hydrocarbon. Filter the rubber bromide into a tared asbestos Gooch crucible and wash the precipitate thoroughly with 95% ethyl alcohol. Dry the crucible to constant weight in a vacuum oven at 65°C. (requires about 1 hour). Cool in a desiccator and weigh. The weight of the rubber bromide when multiplied by the conversion factor (0.301 for guayule) will be the rubber hydrocarbon weight.

b. Rubber Hydrocarbon and Resin in Guayule Plant Material. The most important analysis as far as factory and pilot plant control is concerned is the analysis of shrub for rubber hydrocarbon. An error of 0.6% in rubber hydrocarbon on the basis of 100 parts of dry shrub can cause an error of 5% in rubber hydrocarbon accountability (assuming the shrub contains 15% rubber hydrocarbon). The modified Spence-Caldwell triple solvent method, which was in use at the start of the program, was based on the principle of extracting acid-steam hydrolyzed tissue with boiling water, acetone, and benzene respectively. The benzene extract was evaporated and weighed as pure rubber hydrocarbon. This method always gave low results. The reasons are as follows: (1) the extraction was never complete as could be shown by staining the extracted tissue with an accepted rubber differentiating stain, then examining the tissue microscopically. Hammermilling does not rupture all of the plant cells and some rubber is trapped inside. (2) Rubber of very low molecular weight is dissolved during the acetone extraction and is "lost." (3). Hammermilled tissue is subject to channeling and packing.

There are other disadvantages to the triple solvent method which do not necessarily lead to low results. The rubber film is occasionally contaminated as evidenced by darkened color. The rubber film is not stable and may pick up weight through oxidation even when dried in a vacuum oven. The method is time-consuming requiring 3 days for an analysis.

Many experiments were performed in an effort to improve the existing triple solvent method. It was shown that 95% ethanol was a better resin solvent than acetone because it extracted more resin and less low molecular weight rubber. Other solvents such as methyl ethyl ketone and ethanol toluene azeotrope were tried but it was found that they were no better than acetone.

Several experiments on shrub drying before analysis indicated that over-drying causes a loss in reportable rubber hydrocarbon. The loss is apparently due to formation of acetone and alcohol soluble rubber (See Table 1).

It was found that acid-steam hydrolysis as recommended by Spence and Caldwell was not necessary. In fact, this pretreatment gave erratic results because of channeling and packing.

Sheeting tissue through smooth rolls is a better means of comminution for analytical work than is hammermilling. More cells are ruptured resulting in the release of more rubber. More uniform samples can be taken from sheeted tissue than from hammermilled tissue.

The mechanical shaking of tissue with pebbles and 1% trichloroacetic acid in benzene is a rapid and convenient procedure for putting the rubber into solution. The rubber goes into solution in as short a time as 2 minutes as compared to 16 hours by triple solvent procedure. Rubber hydrocarbon is then determined by bromination. Resin is not determined in this procedure. When resin determination is necessary, it should be carried out by ethanol extraction on a separate sample.

(1) Modified triple solvent method. Because most of the shrub analysis data were obtained by the modified triple solvent method, it is given here in detail.

(a) Preparation of sample. Immerse plants in boiling water for 15 minutes and shake off leaves. Pass through an ensilage chopper and through 1/2-inch screen on rotary fly knife cutter. Dry at 65°C in a forced air circulation oven until the moisture is reduced to 2 - 6 percent (4 hours). Grind in a laboratory hammermill through first a 5 mm. screen and second through a 3 mm. screen and remove a 10-gram aliquot for determination of moisture by drying for 1 hour at 110°C.

(b) Extraction. Transfer a 2-gram sample to a glass extraction thimble in which the perforations have been covered with a plug of pyrex glass wool. Insert a second glass wool plug above the sample, attach the thimble to a block tin condenser, and connect to a tared 400 ml. ASTM (Designation D-297-43T) rubber extraction

Table 1. Changes in Analyses of Guayule Shrub in Drying at 65°C. Comparing Acetone and Ethanol as Resin Solvents.

Drying Time 65°C.	Acetone Extracted				Ethanol Extracted			
	% RHC	Standard Deviation	% resin	Standard Deviation	% RHC	Standard Deviation	% resin	Standard Deviation
Air dried 96 hours at room temperature	16.11	.07	---	---	16.46	.08	10.82	.14
12 hours	16.25	.11	---	---	16.68	.09	10.14	.12
18 hours	16.23	.05	9.62	.12	16.70	.08	10.32	.14
24 hours	15.98	.11	---	---	16.47	.09	10.08	.08
36 hours	15.92	.09	---	---	16.64	.15	10.56	.04
48 hours	15.85	.08	---	---	16.28	.17	10.79	.12
72 hours	15.77	.05	---	---	16.09	.08	10.75	.07
96 hours	15.37	.13	---	---	16.00	.20	10.59	.05

Note: Shrub variety 593, dryland, 6-years old, parboiled, cut through Ball & Jewell 1/2-inch screen. Rubber hydrocarbon determined by film weight. Each value is average of 12 determinations.

Table 2. Comparison of Resin Solvents and Their Effect on Rubber Hydrocarbon Determination

Resin Extracted 18 hours with	Shrub Dried 12 hours @ 65°C.				Shrub Dried 24 hours @ 65°C.			
	% RHC	Standard Deviation	% Resin	Standard Deviation	% RHC	Standard Deviation	% Resin	Standard Deviation
Acetone	16.45	.30	9.82	.19	15.95	.25	10.29	.18
Methylethyl ketone	16.02	.38	10.92	.14	15.62	.53	11.15	.14
Ethanol toluene azeotrope	16.30	.27	10.75	.12	16.09	.31	11.20	.16

Note: Shrub variety 593, dryland, 6-years old, parboiled, cut through Ball & Jewell 1/2-inch screen. Shrub dried and then stored 5 months. Each value is average of 12 determinations.

flask containing approximately 100 ml. of water, and extract for 4 hours. Remove water from thimbles by suction. Extract for 16 hours with 100 ml. of 95% ethyl alcohol. If resin is to be determined, evaporate ethyl alcohol on a steam bath and dry extract in vacuum oven (28-30 inches vacuum) for 1 hour at 100°C. Extract in a second tared flask for 16 hours with 100 ml. benzene. Evaporate benzene on a steam bath and dry rubber film in vacuum oven for 1 hour at 100°C. After the solvents are driven off the flasks are weighed for determination of alcohol and benzene soluble materials.

(2) Shaker method. This is the procedure now recommended for determining rubber hydrocarbon in shrub and one that was developed about a year before the project was terminated.

(a) Preparation of sample. Immerse plants in boiling water for 15 minutes and shake off leaves. Pass through an ensilage chopper and through 1/2-inch screen on rotary knife cutter. Dry at 65°C. in a forced air circulation oven until the moisture is reduced to 2 - 6 percent (4 hours). Crush between closely set corrugated rolls ten times. Sheet between closely set smooth rolls for 10 passes, rolling the sheet after each pass, and inserting the rolled sheet endwise. Remove a 10-gram aliquot for moisture determination. (If dry, finely-divided tissue is available, all steps may be omitted until the sheeting step). Tissue which is low in rubber may powder instead of sheet, but may be sampled with equal accuracy.

(b) Extraction. Weigh analytically an aliquot calculated to give a rubber solution of 1.2 - 2.0 mg./ml. (1.5 g. for tissue containing 12-20 percent rubber hydrocarbon) and place in a heavy walled 250 ml. centrifuge bottle. Add approximately 100 grams of 5-10 mesh pebbles and exactly 150 ml. of 1% solution of trichloroacetic acid in benzene. Stopper and place on a mechanical shaker lengthwise with respect to the shaking movement. Shake for 10 minutes and centrifuge 15 minutes at 2000 RPM.

(c) Bromination. Pipet a 25 ml. aliquot of the clear supernatant solution (containing 30 to 50 mg. of rubber hydrocarbon) into a 250 ml. beaker. Brominate as previously described. Multiply the weight of rubber hydrocarbon found by the dilution factor of 6 and divide by the moisture-free sample weight to obtain percent rubber hydrocarbon.

c. Composition of Acetone-Water Extracts. The work on deresinating shrub and worms to obtain a high-grade rubber necessitated development of a method for analyzing miscellas. Shrub miscella contains acetone, water, acetone solubles and water solubles. Worm miscella does not contain water solubles. The first method which was developed depended upon distillation but it was found that acetone was lost even when the receiver was cooled with ice water. The second and preferred method is given below.

(1) Total solids and sample weight. Pipet 25 ml. of the well-mixed sample at 25°C into a tared covered weighing dish. Weigh to obtain the sample weight. Evaporate to apparent dryness on a water bath and then dry to constant weight in a convection oven at 65°C. This weight represents the amount of total solids.

(2) Water solubles. Pipet a 25 ml. aliquot of the well-mixed sample onto a 3-gram piece of absorbent cotton supported by a piece of heavy filter paper on a watch glass. Evaporate to dryness on a steam bath and transfer to a large siphon cup, placing the piece of filter paper in first. Remove any solids adhering to the watch glass with a small piece of cotton and add to the siphon cup. Extract for 4 hours with 100 ml. of distilled water, using a tared 400 ml. extraction flask. Dry to constant weight in a convection oven at 65°C. (approximately 16 hours). The weight of the residue minus a blank run on the cotton and filter paper represents the water soluble material.

(3) Acetone solubles. Acetone solubles are equal to total solids in the case of worm resin. For shrub resin the acetone solubles equal the total solids minus the water solubles.

(4) Acetone. The specific gravity of the sample at 25°C. is read with a hydrometer. The specific gravity is corrected by the following equation: Corr. Specific Gravity = Sp. g. reading - (% Total Solids)(.0019) (.0019 is an experimental factor to correct for the effect of resin on the specific gravity of miscella). Weight percent acetone is read from a graph of specific gravity versus weight percent acetone or from Table 3. Weight percent acetone is corrected by the following equation:

Corr. Weight % Acetone = (100 - % Total Solids)(Wt. % Acetone reading)

(5) Water. Weight percent water in miscella is found by the following equation:

Wt.% Water = (100 - % Total Solids) - Wt. % Acetone

d. Rubber Hydrocarbon and Insolubles in Crude Rubber. Several experiments were carried out in an effort to improve the accuracy and precision of the rubber hydrocarbon analysis for resinous and deresinated guayule rubber. One such experiment consisted of dissolving the rubber in benzene containing trichloroacetic acid, centrifuging the insolubles, evaporating the benzene-rubber solution to a film, and extracting the resin from the film with alcohol. This method gave erroneous results because of the formation of alcohol soluble rubber. Other experiments failed for similar reasons.

After the accuracy and precision of the bromination procedure had been improved, further efforts to improve the rubber hydrocarbon determination in raw rubber were considered unnecessary for the time being.

(1) Alcohol - Benzene Insolubles. Pass the raw rubber sample 6 or 8 times through close-set, cold milling rolls to blend the material and break down gel rubber, and sheet out thinly. Determine moisture on an aliquot (See section on moisture in raw rubber). Weigh analytically a 0.5 g. aliquot into a tared 70 ml. centrifuge tube. Add 50 ml. of 1% trichloroacetic acid in benzene. Let the mixture stand for 48 hours in subdued light with occasional stirring (or stopper and mechanically shake for 4 hours). Warm the mixture by placing the tube in a beaker of hot water. Centrifuge for 20 minutes at 2000 RPM and decant the supernatant benzene-rubber solution into a 250 ml. volumetric flask. Wash the residue in the tube twice with 40-50 ml. of benzene, thoroughly breaking up the residue with a stirring rod, and

Table 3. Specific Gravities of Water-Acetone Solutions made up to 100 ml. Volume (25°C.)

Volume Acetone ml./100 ml.	Volume Water ml./100 ml.	Weight Acetone g/100 ml.	Weight Water g/100 ml.	Total Weight g./100 ml.	Weight %	Specific Gravity
0	100	0	99.70	99.70	0	.9970
5	95.3	3.925	95.00	98.93	4.0	.9915
10	90.8	7.85	90.50	98.35	8.0	.9860
20	81.6	15.70	81.30	97.00	16.2	.9745
25	77.0	19.63	76.80	96.45	20.8	.9675
40	63.0	31.40	62.80	94.20	33.6	.9460
50	53.3	39.25	53.15	92.40	42.5	.9295
55	48.5	43.20	48.35	91.55	47.2	.9200
60	43.5	47.10	43.35	90.45	52.0	.9100
75	28.2	58.85	28.10	86.95	67.8	.8730
90	12.1	70.60	12.05	82.65	85.4	.8280
95	6.2	74.60	6.18	80.78	92.4	.8070
100	0	78.50	0	78.50	100.0	.7850

centrifuging each time; add the wash benzene to the contents of the volumetric flask. The benzene-rubber solution in the volumetric flask is then used for the determination of rubber hydrocarbon. Wash the residue in the tube with two portions of alcohol and dry the tube and contents at 100°C for 1 hour. Cool in a desiccator and weigh. The weight of the residue represents the alcohol-benzene insolubles matter in the sample.

(2) Bromination. Make the benzene-rubber solution to volume, and pipet a 25 ml. aliquot into a 250 ml. beaker. Proceed with bromination as described in the section on Rubber Hydrocarbon by Bromination.

(3) Calculations.

% Insolubles = (Wt. of Residue) (100) ÷ Wt. Sample, MFB
% RHC = (Wt. ppt.) (.301) (10) (100) ÷ Wt. Sample, MFB

o. Dirt in Raw Rubber. Dirt and foreign material are generally considered to be very deleterious to the production of high grade rubber goods. Products particularly susceptible to dirt are thin-walled articles, rubberized goods, inner tubes and other pneumatic equipment, insulative, surgical articles, tires, shoes, and ebonite. Physical and mechanical properties which are said to be adversely affected by dirt are: gas tightness, electrical properties, tensile strength, fatigue resistance, tear and abrasion resistance, water absorption, elongation and flex life. Furthermore, dirt acts as a center for localized degradation.

However, there is considerable confusion in the industry as to what constitutes dirt. Dirt is generally defined as particles of foreign matter other than rubber hydrocarbon and dissolved substances which can be separated from the rubber by physical means. For this purpose it is customary to use a 325 mesh screen inasmuch as the main compounding ingredients have a particle size of about 300 mesh (Heinisch). Subcommittee XII of ASTM Committee D-11 has run cross tests on two methods of determining dirt: (1) hot oil method and (2) hot xylene method. Both methods have been tried in this laboratory and have been found to have certain limitations. The hot xylene method appears to be the better. The hot oil method has the advantage of using a larger sample (1 pound) but during the melting process, much of the organic dirt is charred. The hot xylene method works satisfactorily if well masticated rubber is used, but unmasticated rubber is very difficult to dissolve in hot xylene without agitation. Mastication changes the dirt results as will be shown later. Both methods take excessive time.

Dirt is a real problem in guayule rubber. During the pebble milling process plant material and rock flour are incorporated into the rubber. Subsequent pressure treatment, scrub milling, and deresination do not completely free the rubber from plant remains and the insolubles content (total dirt) presently runs about 5%. A small proportion of the total dirt in guayule rubber is "harmful dirt" (over 325 mesh).

A simple and convenient method for measuring "harmful dirt" was developed which has several advantages over both the hot xylene and hot oil methods. The new method is less time consuming, more reliable, and requires less attention on the part of the operator than the older methods.

(1) Procedure. Weigh analytically 5 g. of homogeneous sample, which has been cut into strips approximately $\frac{1}{4}$" x $\frac{1}{4}$" cross section, into a 250 ml. centrifuge bottle. (Note.: Guayule rubber is usually sufficiently homogeneous and soluble to require no mastication.) Add 200 ml. of benzene containing 1% trichloroacetic acid, stopper, and shake on a shaking machine until dissolved (usually 3 hours). Centrifuge 5 minutes at 2000 RPM. Filter through a tared 325-mesh stainless steel screen (Figure 1) and wash residue with 250 ml. benzene. Dry 15 minutes at 100°C and weigh screen plus dirt.

$$\% \text{ Dirt} = \frac{\text{Wt. Dirt} \times 100}{\text{Sample Wt.}}$$

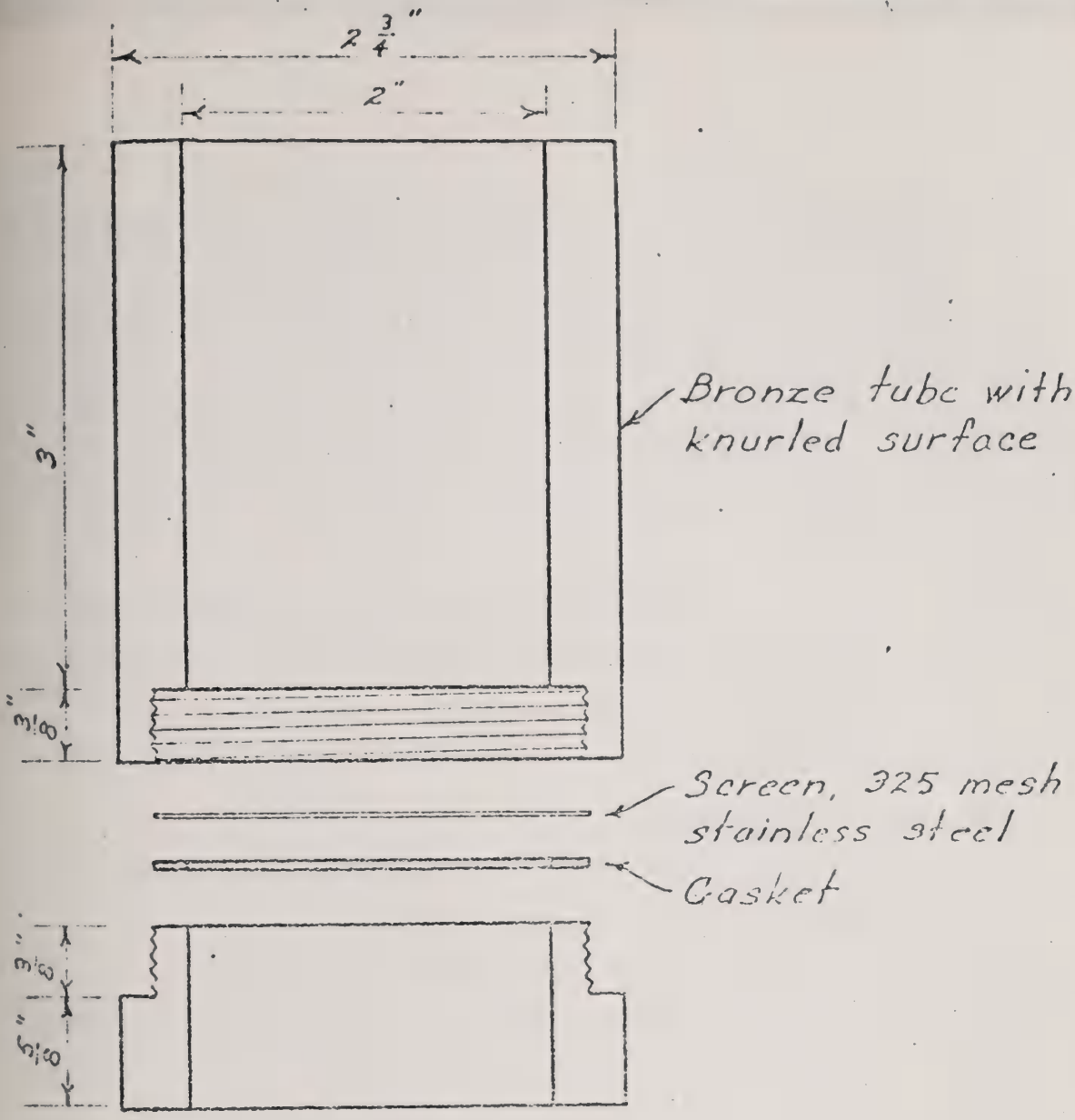
The dirt is hygroscopic and suitable precautions should be taken in weighing. If the rubber is very wet, the dirt should be calculated on a moisture-free basis. Small quantities of moisture may be disregarded. Tests in this laboratory have indicated trichloroacetic acid to be a better solubilizing agent for rubber than RPA No. 3 or Agent K used in other methods. The screens may be cleaned by immersion in hot concentrated nitric acid for 5 minutes without appreciable loss in weight.

(2) Mastication. Mastication has a pronounced effect on dirt content, particularly organic dirt, and should be kept to the minimum necessary to obtain solution in a reasonable time. Table 4 illustrates the relationship between mastication and dirt content. Most of the dirt analyses routinely made

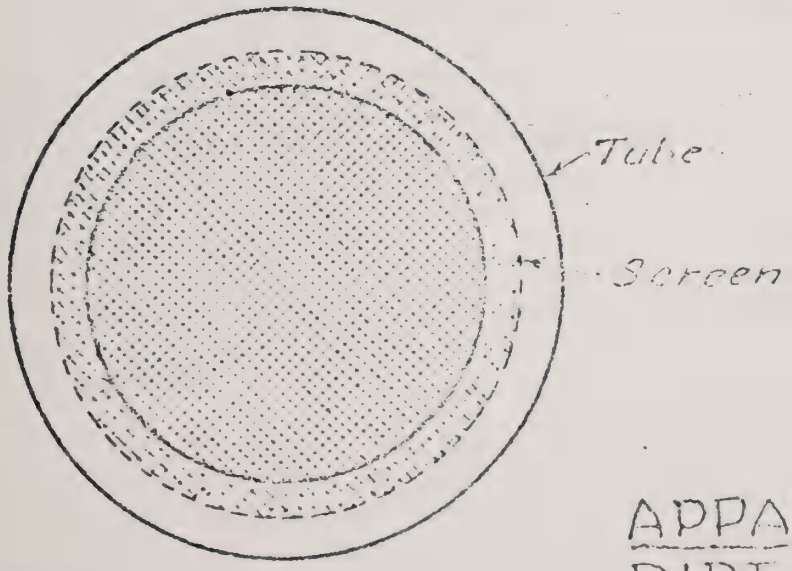
Table 4. Effect of Mastication of Crude Rubber on Its Dirt Content

Passes through 120°F. mill at setting of 0.020"	Dirt Content, Percent			
	#1 RSS	#5 RSS	Deresinated Guayule No. 1	Deresinated Guayule No. 2
0	.12	.30	1.82	.22
1	.10	.30	1.03	.14
5	.08	.20	.85	.12
10	.06	.13	.73	.11
17	.06	.12	.55	.12
30	.04	.12	.55	.06

Each value is the mean of three determinations. The standard deviation for all 72 results was 0.02%. RSS = Hevea ribbed smoked sheet. Deresinated Guayule No. 1 was produced November 14, 1952 by static bed extraction. Deresinated guayule No. 2 was produced in July 1951 by agitated extraction.



VERTICAL CROSS-SECTION



END VIEW

APPARATUS FOR DIRT ANALYSIS

on guayule samples were carried out after 5 passes at a mill setting of 0.020". This was done so that the results would be comparable to those from Hevea smoked sheet in which case at least 5 passes at a setting of 0.020" is necessary in order to dissolve the rubber in a practical length of time. However, the results at 0 passes would probably be more meaningful because it is difficult to correlate laboratory mastication with factory mastication. Mastication differs for each product fabricated. Much of the guayule dirt would be rendered harmless on factory mastication but at this time it is impossible to predict what proportion of harmful dirt might remain in the finished product. Guayule dirt is chiefly organic in nature, having an ash content of approximately 10%.

f. Moisture Determination in Crude Rubber.

(1) Oven drying. Oven methods for measuring moisture in rubber have several disadvantages:

(a) Volatile matter other than moisture is included in the measurement.

(b) Moisture is likely to be trapped in the rubber, unless the sample is in the form of a thin sheet.

(c) Sheeting the sample to a form which can be oven-dried changes the moisture.

(d) Only small samples can be used because of the limitation on sheet thickness

(e) Errors may be introduced through gain in weight by oxidation.

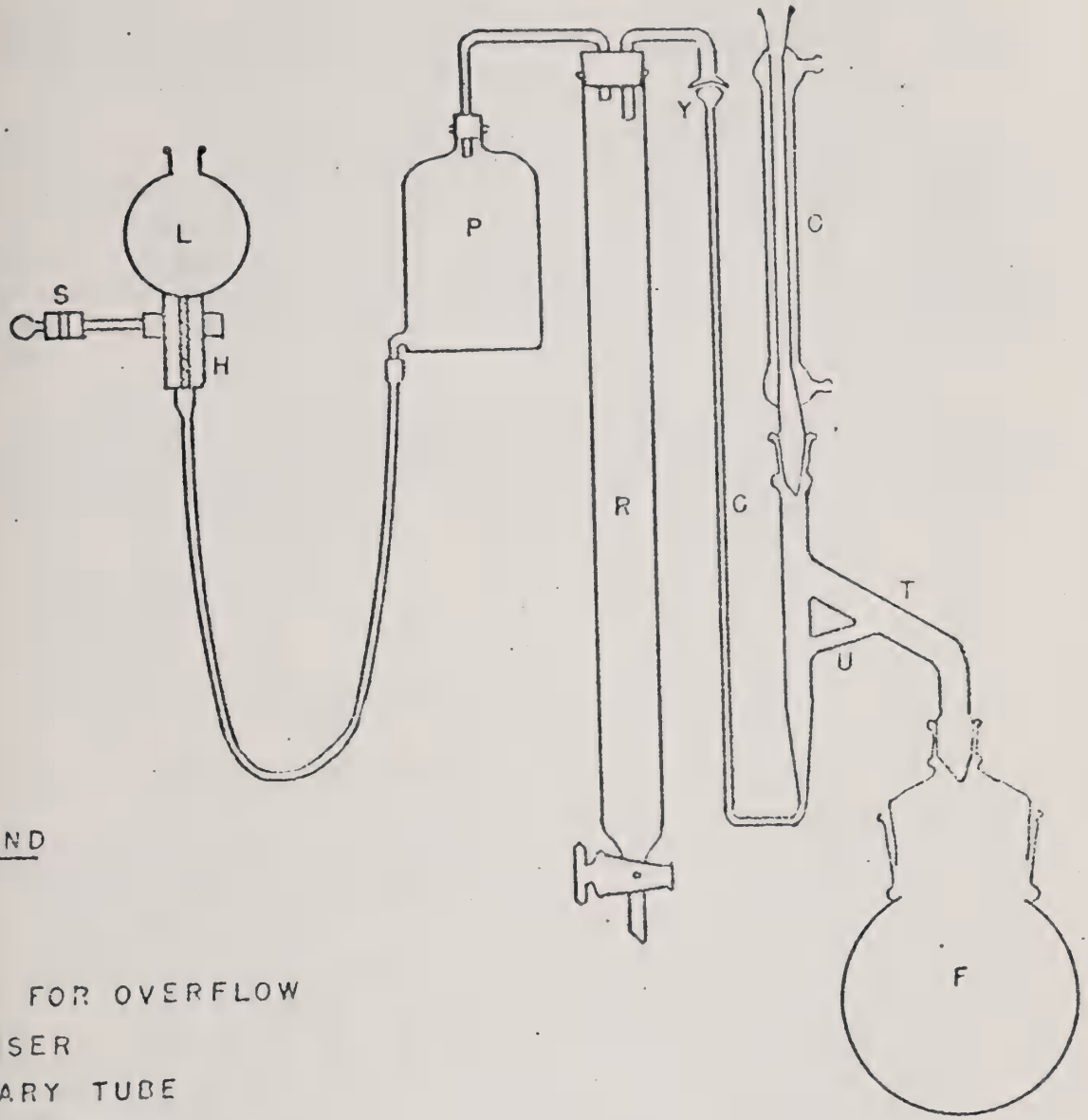
(f) Oven methods are usually time consuming.

The oven method used in the past is as follows:

Weigh accurately a 2 gram aliquot of thinly sheeted sample into a tared moisture dish. Dry in a vacuum oven (28-30-inch vacuum) at 50°C for 16 hours, cool in a desiccator, and weigh. The loss in weight represents the moisture in the aliquot.

(2) Distillation method. Recently a refined distillation method was described which overcomes many of the defects of oven methods. In this method, moisture in the sample is distilled with toluene, collected in a trap, and then drawn into a calibrated capillary and measured. The apparatus is shown in the appended illustration.

The capillary tube, the trap, and the condenser are coated with a thin film of silicone polymer to prevent water droplets from adhering to the walls of the apparatus. The effect of this coating is to reverse the usual water-glass meniscus, and the result is a mercury-type meniscus that is easily seen in the capillary. The silicone coating is applied by pouring a solution, 5 ml. of mixed methylchlorosilanes (Drifilm) dissolved in 100 ml. of dry toluene, into the clean air-dried apparatus and allowing it to stand in contact approximately 15 minutes before pouring out the excess solution. It is important



LEGEND

F FLASK
T TRAP
U TUBING FOR OVERFLOW
O CONDENSER
C CAPILLARY TUBE
Y SPHERICAL JOINT
R GLASS TUBING FOR WASTE
P ASPIRATOR BOTTLE
S RING STAND CLAMP WITH THREADED BLOCK
H BRASS PIPE THREADED TO PASS FREELY THROUGH THE THREADED BLOCK IN S
L LEVELING BULB

APPARATUS FOR MOISTURE ANALYSIS BY DISTILLATION

that the glassware be air dry and not oven dry, as a very thin layer of adsorbed water is essential to form the coating. The apparatus is then air dried and heated overnight in an oven at 105°F.

The capillary is calibrated by adding, progressively, weighed increments of water to the tapered portion of the trap, which has been filled previously with dry toluene up to the overflow tube. After each increment has been added, the water in the trap is raised up into the capillary by lowering the leveling bulb. The height of the water column is measured with an accurate metric scale and the leveling bulb raised to return the water to the tapered portion of the trap. Another weighed increment of water is added and the process repeated.

Because toluene is present in the trap, the water column is confined between two columns of toluene. This prevents evaporation loss and also aids in obtaining a sharp mercury-type meniscus at both ends of the water column. If the capillary is uniform, a simple weight to length factor is all that is required.

$$\text{Calibration Factor: } C = \frac{D}{B}$$

B = the length of the water column in millimeters.

D = the weight of the water in grams

Cut slices not more than one-half inch in thickness from the sample of rubber for which a moisture determination is to be made. Weigh to the nearest 0.1 gram a specimen comprising approximately 25 grams. Place the weighed specimen in a 2-pound size kraft paper bag which has been refluxed in toluene for 3 hours (Note: The paper bags may be stored under toluene after refluxing, but should be refluxed again for at least 30 minutes just prior to making a run). Place the bag in the distilling flask and add 500 ml. of toluene which has been dried by refluxing. Connect the distilling flask to the apparatus using silicone grease to seal all ground glass joints. Heat the flask with an electric mantle. Distill the toluene as rapidly as possible without excessive foaming. Discontinue the heating after 75 minutes and rinse the condenser with dry toluene. Lower the leveling bulb until the water collected in the trap is drawn into the capillary. Read the length of the column of water in the capillary to the nearest millimeter.

$$\%\ \text{Moisture} = \frac{100(BC)}{A}$$

A = the weight of the sample in grams

B = the length of the water column in mm.

C = the calibration factor

Moisture determinations on both crude and compounded rubbers can be carried out with a high degree of precision by the distillation method. Determinations for the establishment of accuracy have been made at this laboratory that have given a standard deviation of 0.033% for crude rubber and 0.016% for compounded rubber.

g. Resin Content and Acid Number of Crude Rubber. Resin is determined in crude rubber by an extraction procedure with resin solvent. There are two potential sources of error in the procedure: (1) The extraction may not be complete because of the imperviousness of rubber. (2) A small amount of soluble low-molecular-weight rubber may be present or form during extraction. The first error is overcome by halting the extraction, resheeting to expose new surface, and re-extracting. The second error is minimized by using ethyl alcohol as a solvent instead of acetone.

Acid number of crude rubber is defined as the milligrams of potassium hydroxide required to neutralize the free acids in the alcohol extract of 100 grams of material.

(1) Resin. Blend a sample by passing 6 times through close-set, cold compounding rolls. Weigh accurately onto a piece of filter paper 1 gram of crude rubber cut into small pieces. Roll the filter paper into a cylinder so that the pieces of rubber are separated from each other as much as possible. Place the paper and sample in an ASTM siphon thimble and place in an ASTM extraction apparatus using a tared extraction flask containing 100 ml. of 95% ethanol. Extract for 4 hours. Remove sample from thimble and dry for 30 minutes at 65°C. Re-extract for 6 - 8 hours. Remove the extraction flask and evaporate the alcohol on a steam bath. Dry flask for 1 hour at 100°C in a vacuum oven, cool in desiccator and weigh. The weight of the residue is resin.

(2) Acid number. Add 100 ml. of neutral ethyl alcohol to the flask containing the resin residue and warm on steam bath for 10 - 15 minutes to dissolve the free acids present. Titrate with standard alcoholic KOH using phenolphthalein indicator or pH meter (titrate to pH 11.0).

(3) Calculations. % Resin = (Wt. of extract) (100) / Wt. of sample, MFB

Acid number = (ml. of KOH)(NF of KOH)(5600) / Wt. of sample, MFB

h. Ash in Crude Rubber or Plant Material. Weigh accurately into a tared No. 4 porcelain crucible a 5-gram sample of crude rubber or plant material which has been dried at 65°C. Place into a muffle furnace which is at a temperature lower than 200°C. The temperature is allowed to rise to 275°C. From this point on, using a rheostat in the line, the oven temperature is allowed to rise at the rate of 25°C per 1/3 hour until 500°C is reached. This heat is maintained until the majority of the combustible material has burned. Then the oven temperature is raised to 550°C, and the ashing allowed to go to completeness. The ashing procedure takes about 8 hours.

% Ash = (Wt. of ash)(100) / Wt. of sample

i. Trace Metals in Crude Rubber and Plant Material. Active forms of trace metals, particularly copper, manganese and iron, greatly accelerate the oxidation rate of rubber. Maximum safe limits for copper and manganese have been set at 10 and 5 parts per million, respectively, for plantation rubber. Maximum limits for iron have not been set although its deleterious effect is well known.

A comparison is shown in Table 5 of Hevea smoked sheet with a typical sample of resinous guayule rubber. It will be noted that the guayule is

Table 5. Comparison of Hevea Smoked Sheet and Resinous Guayule Rubber with Respect to Trace Metals

		Parts per Million			
		Copper	Manganese	Iron	Ash,%
H.S.S.	Mean	2.66	1.46	62.0	.3536
	Range	2.2 - 3.6	1.4 - 1.5	60 - 64	.346 - .358
	Mean	4.34	5.72	259.2	1.0000
	Range	3.8 - 4.7	5.7 - 5.8	250 - 265	1.000 - 1.000

Each mean is average of 5 determinations. H.S.S. = Honduras smoked sheet. Guayule is typical resinous rubber.

Table 6. Trace Metals in Guayule. A Comparison of Emission Spectrographic Measurements with Absorption Spectrophotometric Measurements.

Material	Mg./100 g. Material					
	Copper		Manganese		Iron	
	E	A	E	A	E	A
Defoliate shrub	.57	1.87	2.60	2.50	114.0	109.1
Bagasse	1.26	1.36	3.72	2.15	120.8	111.3
Deresinated shrub	2.00	2.73	3.00	2.50	132.0	106.0
Resinous rubber	.41	.45	1.20	.69	56.8	64.3
Worm deres. rubber	.23	.34	1.09	.91	60.2	65.6
Shrub deres. rubber	.45	.54	.68	.55	34.8	44.2
Mean	.828	1.215	2.048	1.550	86.43	83.42

E = Emission spectrographic values supplied by Dr. Eastmond of WRRL. Accuracy estimated at ± 15%.

A = Absorption spectrophotometric values obtained with a Coleman Universal Spectrophotometer.

somewhat higher in copper and four times as high in iron and manganese. Some samples of guayule rubber have run as high as 15 ppm of either copper and manganese, although the average for these metals is about 6 ppm each.

Table 6 shows a comparison of the absorption method used in this laboratory with the emission method used at Western Regional Research Laboratory for three types of tissue and three types of rubber. The agreement is reasonably good except for a few discrepancies. The absorption method appears to give somewhat higher copper values, lower manganese values, and about equal iron values. The absorption values are recalculated in Table 7 to put them on a shrub basis. Here it can be seen that only a very small part of the trace metals in the shrub actually end up in the rubber.

An attempt to run a trace metals balance during a typical batch milling is shown in Table 8. The large gain in accountability indicates that trace metals are picked up from the processing equipment (probably mostly rock flour from the milling pebbles) during treatment. Fortunately, most of the contamination appears to go out with the effluent rather than remain in the rubber.

Several improvements in technique have been incorporated into the method of determining trace metals since the Emergency Rubber Project. However, the method is basically unchanged. The method is capable of good precision. Replicate measurements should check to within 1 ppm for copper and manganese under the best conditions. In dealing with such tiny quantities much depends upon the skill and experience of the operator.

(1) Preparation of metals solution. Moisten the 550°C ash (see Ash Determination) with 5 ml. concentrated HCl and boil about 2 minutes. Add 5 ml. of distilled water and filter through acid-hardened filter paper into a 100 ml. volumetric flask, leaving most of the residue which is then evaporated to dryness in the crucible. To the dry residue add 15 - 20 drops of concentrated sulfuric acid and evaporate to sulfur trioxide fumes. Cool, add 1 ml. of 1:1 HCl and warm. Filter and wash into the same flask with five 3 ml. portions of hot 1:100 HCl, then with hot distilled water. Make to volume and mix. This is Solution 1 and must be prepared in a hood.

(2) Iron determination. Pipet similar aliquots of 2 ml. each from Solution 1 into a 25 ml. volumetric flask and test tube. Add two drops of bromophenol blue indicator solution (1 g. bromophenol blue, 3 ml. 0.05 N NaOH, 250 ml. water) to the aliquot in the test tube and titrate with 2 N sodium acetate solution until the color matches that of an equal volume of pH 3.5 buffer solution containing the same quantity of indicator. Add 1 ml. hydroquinone solution (1 g. hydroquinone in 100 ml. of pH 4.5 buffer solution) and 2 ml. of o-phenanthroline reagent (1 g. o-phenanthroline in 400 ml. water) to the aliquot in the volumetric flask, and adjust the pH of the contents to 3.5 by adding the same volume of sodium acetate solution as was found necessary for the aliquot in the test tube. If a turbidity develops upon adjustment of the pH of the aliquot in the test tube, add one ml. of ammonium citrate solution to the volumetric flask before adding the sodium acetate solution. Make to volume, mix, and let stand for 1 hour to assure complete color development. Measure transmittance on spectrophotometer at 500 millimicrons. Determine the concentration of iron from a calibration curve previously prepared from

Table 7. Trace Metals in Guayule. Comparison on Basis of Original Shrub.

Material	g./100 g. Defoliate Shrub	Mg./100 g. Defoliate Shrub.		
		Copper	Manganese	Iron
Defoliate shrub	100	1.87	2.50	109.1
Bagasse	60	,82	1.29	66.7
Deresinated shrub	94	2.57	2.35	99.7
Resinous rubber	18	.081	.124	11.6
Worm deresinated rubber	14	.047	..127	9.2
Shrub deresinated rubber	14	.076	.077	6.2

Table 8. Trace Metals Accountability During Batch Pebble Milling.

Material	Weight in Grams	Mg./100 g. Defoliate Shrub		
		Copper	Manganese	Iron
Shrub, 6 yr. old	100.0	1.87	2.50	109.1
Resinous rubber	18.7	.084	.126	12.0
Bagasse	58.3	.950	1.255	67.7
Effluent solids	23.0	2.070	2.020	64.7
Total	100.0	3.104	3.401	144.4
Accountability gain, Wt.		1.234	.901	35.3
Accountability gain, %		66.0	36.1	32.4

similarly treated standard solutions of known concentration. To prepare standard iron solution of 1 mg/l., dissolve 1 gram of electrolytic iron in 50 ml. of 10% sulfuric acid, warming if necessary. Cool and dilute to 1 liter with distilled water.

(3) Copper determination. Pipet a 50 ml. aliquot of Solution 1 into a 125 ml. glass-stoppered separatory funnel. Add 10 ml. of 15% citric acid solution. Drop a small piece of litmus paper into the funnel and neutralize with 1:1 ammonium hydroxide solution. Add 4 ml. of ammonium hydroxide solution in excess (pH = 9.5). Add 20 ml. of carbamate reagent (1 g/l of sodium diethyl dithiocarbamate in distilled water) and 4 ml. of carbon tetrachloride. Shake mixture vigorously. Allow 20 minutes for layers to separate. Shake down carbon tetrachloride from upper surface, dry stem of separator, and draw off carbon tetrachloride into a dry 25 ml. volumetric flask. Repeat extraction three more times or until carbon tetrachloride layer is colorless. Make to volume and add about 1.5 g. anhydrous sodium sulfate. Stopper and shake. Measure transmittance of the dehydrated yellow carbon tetrachloride solution on the spectrophotometer at 435 millimicrons. Transmittance should be measured within 2 hours as a slight turbidity may develop in some samples. Read concentration from a calibration curve previously prepared from similarly treated standard solutions of known concentration. To prepare standard copper solution of 1 mg./ml, dissolve 3.928 g. $CuSO_4.5H_2O$ in distilled water and dilute to 1 liter. Standardize gravimetrically by electrolytic deposition.

(4) Manganese determination. Pipet 25 ml. of Solution 1 into a 150 ml. beaker. Add 2.0 ml. concentrated sulfuric acid, cover with ribbed watch glass, and carefully evaporate until sulfur trioxide fumes have appeared for 5 min. Add 4 ml. of 2 N nitric acid to the beaker, warm to dissolve salts, and transfer to a 15 ml. centrifuge tube graduated at 10 ml. Add 1 ml. 85% phosphoric acid to the tube and wash the beaker with distilled water, keeping the total volume under 11 ml. Stir the solution thoroughly. Place in a boiling water bath and add about 200 mg. potassium metaperiodate. Stir until all of the salt has dissolved and leave in the bath for 1 hour. Cool and make to volume (10.0 ml.). If silica separated out during the first evaporation, centrifuge 5 minutes at 2000 RPM just before transferring to absorption cell. Measure transmittance in spectrophotometer at 530 millimicrons. Read concentration from a calibration curve previously prepared from similarly treated standard solutions of known concentration. To prepare standard manganese solution of 1 mg./ml., dissolve 2.878 g. potassium permanganate in distilled water and dilute to 1 liter. Standardize with sodium oxalate.

j. Total Solids in Liquids. Frequently it was necessary to measure the total solids in unstable liquors or materials which formed a skin on evaporation. The following methods were used in these instances.

(1) Solutions high in sugars. Place 5-10 grams of clean, acid-washed sand that has been ignited at 800-900°C for 3 hours in a 50 ml. evaporating dish. Heat the dish at 110°C for 20 minutes and cool in a desiccator. Weigh the dish and sand along with a short stirring rod. Pipet 20 ml. of the well-mixed solution into the dish. Place the dish on a steam bath and evaporate nearly to dryness. Stir to insure mixing of the thickened solution with sand. Put the dish in a vacuum oven at 70°C and dry to constant weight (12 hours). Cool in a desiccator and weigh. The total solids may be reported as grams of material per 100 ml. of solution.

(2) Quick method. Place 5-10 grams of clean, acid-washed sand that has been ignited at 800-900°C for 3 hours in a 50 ml. evaporating dish. Heat the dish and sand for 20 minutes at 110°C and put in a desiccator to cool. Weigh the dish and sand. Pipet a 20 ml. aliquot into the dish. Place the dish in a 110°C circulating air oven and dry for 3 hours. Cool in a desiccator and weigh.

k. Rubber Hydrocarbon and Resin in Water Dispersions. Analysis of water dispersions of guayule rubber presented a problem which was never fully solved because of the wide variety of samples and concentrations encountered. The rubber hydrocarbon concentration varied from a few milligrams per liter for effluent samples through 1-2% for dilute latex dispersions, up to 60% for concentrated latex. Sampling difficulties were frequently present, particularly with effluent samples. The latex work was halted in 1949 so that analysis of latex ceased to be a pressing problem.

(1) Disperson concentration. In analyzing effluent samples it is necessary to dispose of large quantities of water. The samples cannot be filtered because the large amount of fine plant solids rapidly blind the filter. Experiments were conducted with clarifying agents such as calcium oxide, calcium chloride, and lead acetate with and without heating. Lead acetate, when added at the boiling point, clarified the solutions quite well but later interfered with the rubber hydrocarbon determination by bromination or film method. Calcium chloride was better than calcium oxide but neither was as effective as lead acetate. Filter cel proved to be too bulky. Further research might reveal a satisfactory method for clarifying dilute dispersions for analysis but the present work indicated that excessive man hours might be involved.

(2) Determination of Rubber and Resin. A method was developed based on the evaporation of the water which could be used for all concentrations. After evaporation the solids are extracted for resin and rubber. This method, while time-consuming, does not require much of the operator's time.

Table 9 compares acetone with alcohol as resin solvents in their effects on rubber hydrocarbon by benzene film and bromination.

Table 9 Analyses of Effluent for Rubber Hydrocarbon

Treatment	Mg./100 ml. Mean	Standard Deviation	Coefficient of Variance, %
Acetone, benzene film	3.35	.65	19.30
Acetone, bromination	3.07	.86	27.84
Alcohol, benzene film	3.80	1.03	27.01
Alcohol, bromination	3.48	.87	24.93

Each mean is the average of 24 determinations.

There isn't much choice between treatments. The coefficient of variation for all four treatments when applied to shrub analysis is approximately 1.5%. Therefore, it appears that most of the error occurs in sampling. Until the sampling of effluent is greatly improved there is not much point in trying to improve the method further. Fortunately, from the standpoint of rubber accountability, the rubber in the effluent is a very small part of the total.

Transfer a measured aliquot of the well-mixed sample estimated to contain approximately 250 mg. of rubber hydrocarbon (1 qt. in the case of effluent) to a beaker of appropriate size. Evaporate to dryness in a circulating air oven at 90°C (usually 24-48 hours) to insure coagulation of the rubber. Soak for a few minutes in 50 ml. of distilled water which has just been previously heated to boiling. Transfer to an extraction thimble containing a glass wool pad. Place a glass wool pad on top, place the thimble in a siphon cup, and extract with water for 4 hours in a modified ASTM apparatus. Extract with ethyl alcohol and benzene as given in the section on Rubber Hydrocarbon and Resin in Guayule Plant Material. Determine rubber hydrocarbon by film weight or bromination. Report results as Mg./100 ml.

1. Determination of Bromine in Rubber Bromide. In order to demonstrate the value of bromination as a means of determining rubber hydrocarbon, it was believed highly desirable to establish the purity of the rubber bromide formed. Willits et al attempted this by analyzing the bromide for carbon and hydrogen. They obtained results lower than theoretical. In this laboratory, the problem was attacked by analyzing the rubber bromide for bromine content since bromine is the major constituent (70%). Results obtained with the Parr bomb and Carius methods were disappointing because rubber bromide is difficult to combust. The method described by Peters et al using the Shell-Braun apparatus was tried with good results. In this method the sample is vaporized in a stream of air and the vapors are oxidized over quartz particles at 950° to 1000°C. The halogen is absorbed in an alkaline peroxide solution and is then determined by volumetric analysis. The method is accurate to about 0.1% bromine when analyzing rubber bromide.

(1) Reagents.

(a) Sodium hydroxide, 25%. Dissolve 500 g. C.P. sodium hydroxide in 1400 ml. distilled water. Cool in water bath over night and dilute to 2 liters with distilled water.

(b) Hydrogen peroxide, 6%. Dilute 200 ml. C.P. hydrogen peroxide (30%) to 1 liter.

(c) Sodium carbonate, 2.5%. Dissolve 50 g. C.P. sodium carbonate in distilled water and dilute to 2 liters.

(d) Hydrazine sulfate, C.P.

(e) Nitric acid, 35%. Dilute 415 ml. C.P. concentrated nitric acid to 1 liter with distilled water. Aerate to remove oxides of nitrogen.

(f) Ferric alum indicator solution. Dissolve 350 g. C.P. ferric ammonium sulfate crystals in 1 liter of distilled water. Add 200 ml. of 30% aerated nitric acid.

(g) Sodium chloride. Since this is the primary standard, the C.P. product should be recrystallized. Prepare a saturated solution using C.P. sodium chloride and distilled water. This solution is filtered and concentrated hydrochloric acid is added to the filtrate. The precipitated salt is filtered off with suction, washed with water, dried, ground to a powder, and heated in an electric furnace at 500° - 600°C to constant weight.

(h) Silver nitrate solution, standard 0.1 N. Dissolve 17 g. C.P. silver nitrate in distilled water and dilute to 1 liter. Store in a dark bottle. Standardize volumetrically against 0.14 to 0.15 g. pure sodium chloride using the Mohr method which is as follows: Dilute chloride with 25-50 ml. distilled water into a small Erlenmeyer flask. Add 1 ml. of 5% potassium chromate solution and slowly titrate with 0.1 N silver nitrate solution swirling constantly until first permanent color deviation from pure yellow of the suspension is obtained. Determine indicator blank by adding 1 ml. of indicator to 50 ml. distilled water and titrate until the color of the blank matches that of the solution titrated. The blank is deducted from the volume of silver nitrate used in the titration. Calculate normality of the silver nitrate.

(i) Potassium thiocyanate solution, standard 0.05 N.

(2) Procedure. Place 40 ml. 25% sodium hydroxide and 60 ml. distilled water into first scrubber of the Shell-Braun apparatus. Into second scrubber place 25 ml. of 6% hydrogen peroxide and 75 ml. distilled water. Replace scrubber solutions daily.

Pipet 25 ml. of 2.5% sodium carbonate and 10 ml. 6% hydrogen peroxide into primary absorber and mix by turning on vacuum pump for a few minutes. Pipet 10 ml. of this solution into filter tube.

Assemble apparatus and adjust vacuum control valve so that air is drawn through absorbers at a rate of about 2.5 liters per minute. Heat combustion tube (filled part) to a temperature of 950 - 1000°C while air is being drawn through tube at required rate. Maintain temperature and air control at this rate during rest of analysis.

Break connection between air scrubbers and quartz tube and insert combustion boat and weighed sample at distance of 140 to 150 mm. in quartz tube. Use wire hook to put in position. Reconnect air scrubbers, place Fisher burner

under quartz tube at point near entrance end and vaporize sample at a slow constant rate by gradually moving burner toward boat. After sample has been vaporized, move burner slowly along tube so as to vaporize any material condensed between boat and furnace.

Place burner directly beneath boat and place nichrome gauze on tube above burner. Turn on oxygen supply and adjust flow until air from the atmosphere just stops flowing through scrubber. Burn all residual carbon by moving burner and gauze along the tube up to the furnace. Turn off oxygen supply and adjust heat input to the furnace so latter will not overheat after oxygen is shut off.

Disconnect quartz tube from the absorber. Stopper the absorber opening with cork and allow a vacuum (20 to 25 in.) to develop in the absorber. Close vacuum control valve and slowly bleed air into system through air inlet valve, allowing the liquid to be drawn from the secondary absorber into the lower U-tube. As the pressure equalizes remove spray trap and rinse it with distilled water, collecting the washings in the filter tube. After all the liquid has been drawn into the lower absorber, rinse filter tube thoroughly, using a total of not more than 20 ml. water. Finally, remove filter tube and wash the ground joint inside and out.

Transfer the liquid quantitatively to a 250 ml. or 500 ml. Erlenmeyer flask depending on the amount of halide present (0.2 mg. or more -500 ml.; 0.2 mg. or less - 250 ml.).

Boil solution 30 minutes to decompose peroxides, taking care not to allow volume of solution to become less than 50 ml. Remove flask from heat, and add 0.1 g. or 0.5 g. of hydrazine sulfate again depending on the amount of halide present, and let cool to room temperature.

Filter the solution if necessary. Acidify with 10 ml. of 35% nitric acid and add 10 ml. nitrobenzene and 3 ml. of ferric alum indicator solution. Add 0.4 to 0.6 ml. 0.05 N thiocyanate solution from a burette.

Swirling continuously, titrate with 0.1 N silver nitrate solution until the red ferric thiocyanate color is destroyed, then add 2 to 5 ml. in excess. Stopper flask tightly and shake vigorously to coagulate and remove the precipitate from the aqueous phase. Without refilling burette, titrate with 0.05 N thiocyanate until a slowly fading red color is obtained. Stopper flask shake vigorously for 20 to 30 seconds, and continue titration to a red color which does not fade on further shaking.

$$\% \text{ Br} = (\text{Ml. Ag NO}_3)(\text{Normality})\ (.07992)(100)/\text{wt. of sample.}$$

m. Determination of Carbon and Hydrogen. Carbon and hydrogen were determined on purified rubber films and resin fractions. Table 10 shows the analysis of a purified guayule film. A benzene-rubber solution was prepared by successively extracting guayule shrub with water, acetone, ethanol, and benzene. Films were prepared by evaporation on a water bath and were stored in the dark in a vacuum desiccator until analyzed.

Table 10. Analysis of Purified Guayule Rubber for Carbon and Hydrogen.

Component	% Found	% Theoretical	% of Theoretical
Hydrocarbon	99.49	100	99.49
Carbon	87.69	88.16	99.47
Hydrogen	11.80	11.84	99.48

Each value is the mean of 3 determinations.

(1) Procedure. A carbon and hydrogen combustion train with electrically heated furnaces was set up. A weighed sample of rubber (approximately 0.1 g.) is burned in the combustion tube through which is passed a slow stream of oxygen (12 ml./min.). The combustion usually takes about 3 hours. Proper burning gives complete combustion to carbon dioxide and water. Water is collected in an absorption tube containing "Drierite", and carbon dioxide is retained in the tube containing "Ascarite".

If the rubber catches on fire there is momentarily a deficiency of oxygen. This results in the formation of carbon monoxide some of which, not having time to be converted to the dioxide, is not absorbed by the ascarite. To overcome this, the charring end of the sample must be observed carefully to note its appearance. The heating unit may safely be advanced slightly beyond the forward edge when about 1/8-inch has lost all of its gloss.

n. Determination of Hydroperoxides. Hydroperoxides are formed when rubber is oxidized. Methods have been developed for measuring hydroperoxides. The method used in this laboratory is an adaptation of the method described by Walker and Conway for the determination of hydroperoxides in petroleum products. It is based on extraction and reduction with sodium arsenite.

The method is similar to the method for petroleum products except that benzene is used as the organic solvent instead of petroleum ether, and the extraction apparatus is modified. The extraction apparatus in this method consists of a 500 ml. separatory funnel which is the extraction flask. This is enclosed by a heating mantle adapted for use with a funnel. The heating mantle heats the extraction flask and it is regulated by a powerstat. A condenser connected to the separatory funnel refluxes any vapors which may escape. Nitrogen enters the system by means of rubber tubing extending down the condenser into the extraction flask.

The sample to be analyzed is made up as a benzene-rubber solution. A 2% benzene-rubber solution can be obtained by use of the shaking machine. The rubber and benzene are shaken on the shaking machine for 15 minutes, the solution allowed to stand over night, with 15 minutes additional shaking the next day.

The petroleum method recommends washing the dispensing funnel with ethyl alcohol; but in the present method benzene was used instead, as ethyl alcohol causes interference in the starch end point.

(1) Standard solutions.

(a) Arsenious oxide, 0.1N. Dissolve 4.9450 g. of pure dry arsenious oxide in 50 ml. of 1 N sodium hydroxide. Make neutral or very slightly acid to litmus paper with 1 N sulfuric acid and dilute to 1 liter.

(b) Iodine, 0.05 N. Dissolve 12.7 g. of C.P. iodine and 40 g. of C.P. potassium iodide in 25 ml. of water, and dilute to 2 liters. Standardize against the arsenious oxide solution.

(2) Procedure. Add to the extraction flask 75 ml. distilled water, 20 ml. of 1 N sodium hydroxide, 2 drops of phenolphthalein indicator, aliquot of sample to be analyzed, and 10 ml. 0.1 N arsenious oxide. The dispensing funnel is finally washed with about 25 ml. benzene. Add enough benzene to bring volume of top phase between 50 and 100 ml. Bubble nitrogen through the solution at a moderate rate for 5 minutes, then turn on the heater at a powerstat setting of 75. When refluxing begins, adjust the flow of nitrogen and heat for maximum reflux. If pink phenolphthalein color disappears, restore alkalinity with 1 N sodium hydroxide and add 2 ml. in excess.

Reflux for 45 minutes then acidify mixture dropwise with 10 N sulfuric acid. Turn off heater, and let extraction flask cool to approximately room temperature. Shut off nitrogen and let two phases separate. Withdraw lower phase into 250 ml. separatory funnel, extract 3 times with 25 ml. portions of chloroform and discard chloroform washings. Transfer solution to 500 ml. wide mouth Erlenmeyer titration flask and chill in ice. Add 1 gram sodium bicarbonate and titrate solution with standard iodine. Determine end point by means of starch indicator.

Run a blank determination with each sample or series of samples, using the same amount of reagent and solvents. Calculate the percent active oxygen by means of the following equation:

$$\% \text{ active oxygen} = \frac{8\ N\ (b - s)}{10\ W}$$

where N = normality of iodine solution; b = ml. of iodine solution for blank; s = ml. of iodine solution used for sample; and W = gram. of sample used. If b is less than three times as large as (b - s), repeat determinations after adjusting amounts of sample and standard arsenious oxide reagent.

o. Determination of Antioxidants. Antioxidants are added to guayule rubber to make it more stable in storage. It is important to know how much antioxidant has been added so that the storage properties can be closely controlled. For a while MDT (meta diamino toluene) was added by soaking the rubber in a water solution of the antioxidant. It was found that the concentration of MDT could be determined by titration with hydrochloric acid to pH of 4.00 (pH meter). At this point one of the two amino groups has been neutralized and a sharp inflection in the pH-concentration curve is noted.

However, the use of MDT was discontinued because MDT greatly affected the cure during vulcanization. This appears to be a characteristic of primary amines because Tonox (4,4'- diamino-diphenyl methane) and oxynone (2,4 - diamino-diphenyl methane) do the same thing.

PBNA (phenyl-beta-naphthyl amine) and later, AgeRite White (di-beta-naphthyl-p-phenylene diamine) were used to a considerable extent. Neither antioxidant can be determined by titration. PBNA is used in GR-S and a method is available for determining PBNA based on its ability to absorb light in the ultra violet region. Presumably Age-Rite White would also absorb light in the ultra violet region. However, an ultra violet spectrophotometer was not available to the laboratory so a method based on total solids was developed. The method is not specific as any dissolved solids such as resin interfere. The method does give an estimate of antioxidant in deresinated rubber.

(1) Procedure. Sample deresinated worms (10 - 20 grams) immediately after draining antioxidant solution. Place in tightly sealed tared weighing dish.

Sample antioxidant solution which has been drained (approximately 25 ml.). Place in tightly sealed tared weighing dish.

Weigh dishes containing worms and antioxidant solution. Evaporate both to dryness in explosion-proof oven at 65°C. Cool and weigh the residues in the dishes.

(2) Calculations:

% antioxidant in solution = B(100)/C

B is the weight of total solids and C is the weight of solution drained.

% antioxidant on rubber = D (% antioxidant in solution)/ E

D is the weight of solution retained by the rubber and E is the weight of dry rubber.

p. Inherent Viscosity Measurements. (Molecular Weight). Changes in molecular weight resulting from various processing treatments were followed by inherent viscosity measurements on dilute solutions of rubber in benzene. Absolute molecular weights were not usually calculated because of the disagreement among authorities as to which equation should be used. Staudinger, Magat, Flory, and others have published equations which lead to different results. However, inherent viscosities can be used as a relativemeasure of molecular weight without calculating the absolute values.

Inherent viscosity measurements were shown to be particularly useful in indicating the extent of degradation, as caused by the successive processing steps involved in the recovery of rubber. It was found that much degradation takes place during storage of shrub. Crushing and hammermilling of shrub apparently caused no significant change in inherent viscosity. However, a gradual downward trend occurred through pebble milling, decorking, and scrub-milling. Drying crude rubber with heat is indicated as being very deleterious

and especially so in the case of resinous rubber as compared with deresinated rubber. The cumulative effects of processing may thus contribute appreciably to lowered quality of the final products. Much of the degradation due to drying was shown to be retarded or prevented by addition of antioxidants to the rubber.

(1) Sample preparation. Samples of crude rubber worms (25 to 30 grams, dry basis) were first extracted with cold acetone to remove resins and/or water, depending on previous treatments. Extraction was conducted batchwise using three changes of fresh acetone with frequent shaking over a 2-day period. The extracted worms were dried at room temperature. A 2-gram sample of dried worms was placed into 200 ml. of benzene and allowed to stand for 3 days, with occasional shaking. The solution was carefully examined for the presence of undissolved rubber, then centrifuged to remove all non-rubber benzene insolubles. A 50 ml. portion of the clarified solution was diluted to 250 ml. to give a concentration suitable for the determination of rubber hydrocarbon by bromination. Further dilutions were made, usually 15 to 50 ml., to give a relative viscosity within the range of 1.2 to 1.4. Ordinarily this concentration varied between 0.05 and 0.06 grams per 100 ml. of solution.

In the case of plant tissue, a sample of approximately 25 g. (dry basis) was extracted with acetone in a manner similar to that used for rubber worms. After deresination and drying, the plant material was treated with 300 ml. of benzene and shaken periodically. The solution was decanted after 24 hours, a fresh 200 ml. portion of benzene added, and extraction continued for another 24 hours. This procedure was repeated for a third 24-hour period. By this procedure, approximately 90% of the rubber was extracted. The combined rubber solution was diluted 2:1 for determination of rubber hydrocarbon by bromination, then diluted further to give concentrations appropriate for viscosity measurements.

All extractions with acetone, drying, and solution in benzene were conducted in the dark at room temperature.

(2) Determination of inherent viscosity. Viscosity measurements were made at 25°C $\pm$ 0.05°, using an Ostwald-Cannon-Fenske viscosimeter. The same viscosimeter was used throughout and its calibration checked frequently.

$$n_i = \ln n_r/C$$

where n_i = inherent viscosity

n_r = relative viscosity

= seconds for passage of solution/seconds for passage of benzene

and C = concentration of rubber in g/100 ml.

g. Paper Chromatography. A method has been discovered here for chromatographing crude rubber on silicone-treated filter paper. This new development provides another important means for comparing different elastomers such as

Guayule, Hevea, GR-S, and neoprene with respect to molecular weight distribution, gel content, and various other inherent physical properties and even the effect of certain processing treatments. The full possibilities of the application of paper chromatography to the study of non-polar polymers and especially polyisoprenoids remain to be exploited.

This differential migration of rubber was accomplished by using silicone-treated paper as the stationary phase and certain viscous oxygenated solvents for the more polar, mobile phase. Actually this is a reversal of the conventional procedure of paper partition chromatography in which the paper holds the polar solvent, ordinarily water, as a stationary phase. Most of the experiments were carried out with a micro scale ascending technique. The rubber was applied from dilute benzene solutions to give a line of spots at the edge of the sheet of silicone-treated paper. Many moving solvents were investigated, but the most satisfactory proved to be cyclohexanone and mixtures of butyl diethyleneglycol acetate with cyclohexanone or xylene. Dioctyl sebacate also showed promise. The spots or streaks of partitioned rubber were rendered permanently visible by staining with oil blue NA (Calco).

By means of this technique differential migration patterns have been obtained for various natural and synthetic crude rubbers. Although the shape of these patterns ordinarily precludes the assignment of definite R_f values, the differences noted for dissimilar polymers or even for the same polymer when subjected to different physical or chemical treatments provide an interesting visual means of comparison. The reproducibility of the chromatographic patterns has been found to be good, provided the precautions usual for such work are observed. For example, a definite resemblance was seen in the migration behavior of Hevea and guayule. The somewhat greater mobility shown for guayule probably attests to a lower mean molecular weight, and a much smaller proportion of the poorly soluble gel fraction. The well known effect of trichloroacetic acid in dispersing the gel and otherwise decreasing sol viscosity has likewise been shown chromatographically. Visual demonstration of the physical breakdown which results from the milling of crude rubber has also been shown.

3. Recommendations for Future Research

Analytical methods for guayule research and development are quite well worked out for the most part. A few items which deserve further study or have not been studied at all are listed here.

The determination of rubber hydrocarbon in shrub should be worked on from the standpoint of reducing the time of analysis. Factory control demands frequent and rapid analyses. Possibly a combination of the Traub turbidity method with a shaker extraction might be the answer.

Trace metals should be investigated with the purpose of determining the active metals as well as total metals. The method for copper should be studied to find out why copper results are sometimes erratic and sometimes uniform. Carefully designed sampling experiments and statistical analysis of the data would provide for more accurate interpretation of results.

Effluent analysis needs more study. The method needs improvement and sampling needs investigation.

Studies on the application of paper (and columnar) chromatography to guayule rubber should be included in any future program. Various interesting resemblances and differences in migration patterns have already been shown for guayule with respect to other crude elastomers. Correlation of chromatographic pattern with certain inherent physical properties appears promising and might well be developed later into useful control methods.

Methods should be worked out which would be specific for the determination of antioxidants. This could be done in most cases by taking advantage of the fact that many antioxidants absorb light in the ultraviolet region.

Determination of resin in crude rubber needs further work to find a means of preventing the formation of soluble low-molecular-weight rubber. Addition of an antioxidant might be helpful.

Development of methods of analyses for specific ingredients in water solubles and resin are needed. Since many of the components are still unknown, the opportunity for research in this area is great.

B. Laboratory Processing Studies

The purpose of studying processing on a laboratory scale was twofold. First, it was desired to duplicate pilot plant operations on a small scale so that more experiments could be run with a smaller expenditure of labor and materials. Treatments which did not look promising could then be screened out at the laboratory stage, whereas favorable experiments could be transferred to the pilot plant for further investigation.

Secondly, it was hoped that new processes and equipment could be developed on a small scale before proceeding to pilot-plant-sized experiments. Examples of this second approach where laboratory work preceded pilot plant application, are deresination by agitation and prevention of clumping.

Pressure of other work prevented full realization of desired objectives, but a substantial beginning was made which is reported here.

1. Shrub Preparation and Milling

Since shrub preparation and milling are interrelated unit operations, experiments were designed for their simultaneous investigation. The objectives of the work were: (1) to study the effect of laboratory scale crushing and milling on yield of rubber hydrocarbon; (2) to determine the usefulness of the 6" x 12" washing mill for crushing small quantities of shrub; and (3) to determine the usefulness of the 1-gallon size attritor for milling small quantities of shrub.

The crushing rolls have corrugations 1/16-inch deep. The front roll turns at a speed of 20 r.p.m. and the back roll has a speed of 26.5 r.p.m. Both rolls are filled with scraper blades. The clearance between the rolls was set at 0.002 inch.

The 1-gallon size attritor is a pebble mill with a stationary shell and a vertical shaft with horizontal arms which rotate through the grinding medium. The equipment used was manufactured by the Union Process Co., Akron, Ohio. The tank is stainless steel, and the grinding medium is flint pebbles approximately 3/8" diameter. The maximum speed of 392 r.p.m. was used.

Table 11 shows some results obtained. There was a highly significant

Table 11. Rubber Hydrocarbon Yields as a Function of Crushing and Milling

Experiment	Milling time (Minutes)	RHC Yields (g./200 g. of dry shrub) Number of Times Crushed					
		1	3	5	7	9	11
1	5	2.74	14.28	24.10	29.78		
	10	17.30	26.14	30.23	31.87		
2	5			32.17	31.11	31.40	31.76
	10			31.47	31.74	31.68	31.58
	20			33.23	32.77	31.93	32.41

At .01% level, least significant difference = 1.71
Each value is the mean of 2 replicates performed one day apart. Shrub for Experiment 1 was dryland variety 593, 7 years old, harvested Sept. 25, 1951. Shrub for experiment 2 was similar but harvested on Oct. 8, 1951. Crushing was carried out on a 6" x 12" laboratory wash mill. Milling was carried out in 1-gallon attritor.

difference between number of crushes, between milling times, and in the interaction between crushing and milling. There was some overlapping between the two experiments. Seven crushes and 10 minutes of milling gave the best yields in the first experiment, whereas 5 crushes and 5 minutes milling was satisfactory in the second experiment.

The laboratory attritor was shown to be a useful piece of equipment. The grinding action is fast, and a few minutes in the attritor is equivalent to many hours in a 1-gallon size pebble mill. However, neither the attritor nor small pebble mill duplicate large pebble mills. In the latter, the pebbles are much larger and the distance of fall is greater so that a mashing by impact takes place as well as grinding in the usual sense.

The familiar Waring blendor has been found very useful for milling small samples for laboratory investigations. It has not been feasible to duplicate this type of action on a large scale. The rapid mechanical action tends to degrade the rubber to some extent.

It was shown necessary to parboil foliate shrub in water of at least 90°C to effect leaf removal. Failure to parboil fresh shrub for at least 5 minutes prior to comminution resulted in a molecular weight drop from 195,600 to 93,500 on comminution. Parboiling whole shrub for periods of time ranging from 5 to 40 minutes had no effect on molecular weight of the extracted rubber.

2. Decorking

A miniature pressure vessel of 300 ml. capacity was constructed. A hand-operated pump was attached which allowed hydraulic pressures up to 16,000 p.s.i. to be reached. This device worked extremely well, and decorking was accomplished in a matter of seconds. Laboratory samples of rubber were decorked by means of this equipment.

3. Deresination

Considerable work was carried out on deresination of guayule worms to prepare a high quality rubber. Before this work was started there was some doubt as to whether high grade rubber could be made by worm deresination. Previous investigators had used as a starting material rubber which had been prepared from conditioned shrub. Usually the rubber had been dried at approximately 100°C into sheets before attempting deresination. Therefore, almost without exception the rubber was in an undesirable physical form and badly degraded at the start. With the advent of lush milling and the use of wet worms it became entirely feasible to prepare a high grade rubber by worm deresination.

The laboratory work was divided into three phases, static extractions, dynamic extractions, and diffusion phenomena.

a. Static Extractions. These experiments were designed primarily to determine the distribution of water and resin in the miscella of a counter current extraction. In one series of runs, the apparatus consisted of a glass tube (122 cm. x 5.3 cm.), mounted at about 7° from horizontal, and fitted through rubber stoppers at each end to a regulated withdrawal exit tube at the bottom and an inlet tube at the top. Fresh acetone or miscella was added at the top and miscella fractions were collected at the bottom. The fractions were analyzed for water, acetone, and resin content. Resin content gradually builds up in the miscella as the water content decreases, goes through a maximum and then slowly decreases.

Considerable trouble was encountered with packing and channeling and the work was discontinued. The work did suggest, however, that extraction of static beds up to about 3 or 4 inches in thickness might be feasible. This was later found to be the case and this work is reported under Process Research and Development.

b. Dynamic Extractions. The term dynamic extractions was applied to those cases where solvent to rubber ratios were sufficiently high (>2.5 : 1) to permit vigorous stirring of the system. Under these conditions it would be expected that the concentration of resin in the rubber and in the solvent would reach an equilibrium more rapidly than in a static system.

One series of experiments was carried out by stirring 110 g. of moist resinous worms in 7 liters of acetone. Small samples were taken at intervals and analyzed for resin content. The solvent to rubber ratio of 115 to 1 was set very high so that the system would be essentially uninfluenced by the trace of water and resin introduced in each case. It was found that the rate of deresination was very rapid under these conditions. The deresination was essentially complete at 8 minutes (91 - 95% of the resin removed). After 8 minutes, there was a slow additional deresination which appeared to follow Fick's diffusion law. Up to 8 minutes, the deresination was much too rapid to conform to this diffusion equation. It is postulated that, because of the porous structure of wet worms, most of the deresination takes place by dissolving off absorbed resin from the surface of the rubber. It was found that the temperature effect was very small although deresination took place slightly faster at higher temperatures. Adding water or resin to the acetone did not affect the rate of deresination up to the point of equilibrium but did markedly affect the amount of residual resin left in the rubber.

A series of countercurrent batch extractions was carried out to determine the number of stages necessary to obtain good extraction at a low ratio of acetone to rubber. Two kilograms of hand-squeezed wet guayule worms (46.5% moisture) were stirred with 10 changes of acetone at 30°C. Each stirring period was 5 minutes and each draining period was 2 minutes. The amount of acetone for each stage was 1625 ml. The extraction was repeated with more rubber, reusing the miscella and adding more stages of fresh acetone at the end of the extraction. Additional runs were made in the same manner after removing from the system the miscella from stages 1, 1/3 of stage 2, and all of stage 7, until equilibrium was reached. Equilibrium may be defined as the point at which the amount of water and resin carried in with the rubber during a run is just balanced by the amount of water and resin removed from the system.

Under conditions of equilibrium a materials balance shows 2.5 g. resin/100 g. resin-free rubber in the issuing rubber, 9.25% resin and 4.25% water in the miscella from stage 7; 55.15% water and 0.64% resin in the miscella from stage 1, and 38.45% water and 2.82% resin in the miscella from stage 2. Fresh acetone in the amount of 4.8 g. is needed to produce 1 gram of deresinated rubber not counting evaporation loss. Of this amount, 3.5 g. appears in the miscella and may be recovered by distillation, whereas 1.3 g. may be recovered by collecting the vapors on drying the rubber.

This procedure produced a high grade rubber with low insoluble content (about 3.5%) and a Mooney viscosity of approximately 95. Stirring loosens some of the insolubles which pass through the 80-mesh screen used to separate rubber from miscella. Unfortunately, fine rubber, estimated at 5% of the total, also passes through the screen.

Other solvents were tested in addition to acetone. Among these were furfural, methyl alcohol, ethyl alcohol, isopropyl alcohol, and methyl ethyl

ketone. None of these were as good as acetone because they were less efficient, less volatile, or because the quality of the rubber was adversely affected. Methyl ethyl ketone was interesting, however, because water dissolves in MEK to the extent of 11% only, and the azeotrope also contains 11% water. Because of these properties, it was found possible to deresinate wet worms with MEK azeotrope without diluting the solvent with water as is the case with acetone. Thus, deresination can be accomplished with approximately half the amount of MEK azeotrope as would be required with acetone. A patent was granted on this procedure.

A continuous extractor was constructed out of 4-inch diameter glass pipe fitted with a motor-driven steel scroll and inlet and outlet pipes. The inclination of the apparatus was adjustable. Several runs were attempted but after a short time of operation, rubber would plug the scroll and stall the motor. The experiments were discontinued.

c. Diffusion Phenomena

The diffusion theory derived from Fick's law has been applied to the deresination of guayule rubber. Under the conditions adopted for this study, the diffusion coefficient varies with the solvent but is essentially independent of the thickness of the rubber sheets extracted. This finding is of interest as it permits the direct quantitative comparison of various deresination solvents at different temperatures.

Unfortunately, the diffusion theory could not be tested properly with guayule rubber in the form of worms because of the considerable dimensional variations encountered with the rubber in this condition. However, it was found possible to prepare the resinous guayule in a form better adapted to fundamental study and thus obtain rate data applicable to worm deresination. The form chosen was thethin film obtained by impression of dry resinous rubber in the interstices of stainless steel screens. Since the slab thicknesses of these thin films could be accurately determined and reproduced, a treatment of the extraction data based on the theory of diffusion became feasible. The theory of diffusion as it applies to the extraction of resin from guayule rubber has been published.

The results of this study are summarized in Table 12.

Thus acetone at 25° has a diffusion coefficient of 1.20×10^{-5} sq.cm./min. At slab thickness in excess of about 1 mm. this constant appears independent of thickness in keeping with the diffusion law. At lower thicknesses a deviation from theory exists which is discussed in detail in the published article. The coefficient for acetone is shown to have a rate of change with temperature expressible as follows for values of T near room temperature:

$$D = 2.26 \times 10^{-7} \times T + 5.8 \times 10^{-6}$$

The diffusion coefficients for ethyl alcohol, acetone, and methyl ethyl ketone are in the following approximate ratios, respectively: 0.07, 1.0 and 2.5.

The diffusion coefficients found in this work were determined with thin sheets of dry rubber and, consequently, should be considered most pertinent

to guayule in that form. However, present evidence indicates that these findings have at least limited application to resin extraction from rubber in other physical forms, such as worms. For example, it has been found that the solvents used in this work behave in worm deresination in a manner consistent with their diffusion rates reported here. Also temperature changes have the same rather minor effect on the rate of worm extraction as on thin sheet extractions (a rise of nearly 50°C being required to double the rate with acetone). Temperature can have a decided effect on the completeness of the deresination, depending on the choice of solvent.

Table 12. Diffusion coefficients for deresination of Guayule rubber films with various solvents

Solvent	Thickness cm.	Temperature °C	D, sq.cm/min.
Acetone	0.185	25	1.23×10^{-5}
Acetone	0.137	25	1.16×10^{-5}
Acetone	0.069	25	(a)
Ethyl alcohol	0.066	25	8.06×10^{-7}
Methyl ethyl ketone, water satd.	0.066	25	(a)
Methyl ethyl ketone	0.066	25	3.0×10^{-5}
Ethyl alcohol	0.067	37.5	1.69×10^{-6}
Acetone	0.139	37.5	1.44×10^{-5}

(a) The method for measuring D becomes less accurate at very high or very low extraction rates.

4. Miscellaneous Chemical Treatments

a. Prevention of Clumping. During the work on deresination it was found that if the wet worms were allowed to stand for several hours before deresination, clumping frequently took place which made the rubber difficult or impossible to extract. Experiments were performed to see if clumping could be prevented by addition of various agents. It was learned that addition of 0.5 - 1.0 percent insoluble metallic soap on a dry rubber basis before scrub milling would prevent clumping for several weeks. The metallic soap did not interfere with the deresination in any way. Examples of metallic soaps used are zinc stearate, calcium stearate, and the reaction product of stearic acid and hard water. A convenient method of adding zinc stearate was developed which

consisted of forming a paste with Cerfak N - 100 (Houghton Chemical Co.,) in the ratio of 3 ml. of 2.5 percent Cerfak N - 100 solution to 1-g. zinc stearate. The paste disperses in any quantity of water. This anti-clumping method was tried out on a pilot plant scale with success.

b. Dispersing Resins in Milling. The knowledge that resins are separate from the rubber in the guayule shrub led to extensive investigation of the possibility of dispersing the resins in the milling water during the milling operation instead of deresination. Numerous dispersing agents were tried and it was learned that many detergents and sodium hydroxide and ammonia were effective in obtaining aqueous dispersions of guayule resin. The next step was to apply these detergents to prevent resins becoming incorporated in the rubber during milling. The Waring blendor proved its utility as a laboratory scale mill for the extraction of rubber from comminuted guayule tissue. At first, detergents were added to the milling water. When this failed to lower the resin content of the extracted rubber, other means were tried. The use of a pressure cooker was investigated as a pretreatment to facilitate effective penetration of the detergent solutions prior to Waring blendor milling the shrub. Variables investigated included detergent concentration, pH effect and temperature of milling. In the course of this investigation 194 separate determinations were made utilizing various detergents representative of the three classes, cationic, anionic and nonionic with respect to each of the above variables. Eventually it became evident that the rubber has too strong an affinity for resins for any detergent (at least those investigated) to overcome. In fact it was shown that an aqueous dispersion of guayule resin, wax, or even motor oil when used in the milling media became a source of further contamination rather than a means of deresination. Apparently the more effective the dispersing agent is in freeing the resins from the tissue, the greater the opportunity for the rubber to take up the dispersed resins. This phenomenon has also been observed during the processing of guayule for latex. Detergents or ammonia added during milling of the tissue had an adverse effect on resin content of latex; added later, of course, they proved beneficial.

Another approach to the problem of deresination was based on the belief that the addition of a relatively small quantity of a water immiscible resin solvent to the milling mixture might result in the preferential absorption of the resin and prevent combination of resin with rubber during milling. This actually was the case when substances such as amyl alcohol or tricresyl phosphate were added to milling mixtures in a Waring blendor. Usually 10-25 ml. of the water immiscible resin solvent were added to a slurry of 100 grams of crushed shrub (moist basis) in approximately 400 ml. of water. In some cases, a dispersing agent was also added to facilitate the formation of a good dispersion of the resin solvent. The mixtures were milled 10 minutes in the blendor. The resulting crude rubbers were significantly lower in resin content than the controls. It was found possible to reduce the resin content by 50 percent or more by milling in this manner. However, the practicability of this finding is open to serious question because of the apparent difficulties involved in subsequent recovery of the resin solvent together with the fact that it was not found possible to effect a complete deresination.

c. Decolorization of Guayule Rubber. Crude guayule rubber has a characteristically dark color. This is especially marked in the case of resinous rubber. Deresinated rubber is considerably lighter in color before drying

but darkens during drying. It is known that pure rubber hydrocarbon is essentially white and that the dark color of crude rubber must therefore be due to the presence of impurities. No satisfactory explanation can be given as the cause of the color of crude deresinated guayule, but it is possible that the interaction of traces of iron or other metals with tannin or tannin-like compounds may contribute to the color. Rubber milled out in glass equipment in the laboratory is usually lighter in color than rubber milled in pilot plant equipment. In the case of resinous rubber much of the color may well be due to resins which in themselves are dark in color. Enzyme action is not considered to be a factor because shrub is always parboiled before milling.

Since it is desirable to have a light-colored rubber stock for manufacture of certain products some attention was given to the problem of lightening the color of deresinated guayule rubber. It was learned through correspondence with the Rubber Research Institute of Malaya that a process for removal of the yellow color from Hevea latex had been developed. This entails bleaching of carotenoid pigments by the addition of water emulsified xylyl mercaptan to the latex. Sodium bisulphite was also reported to be used for the prevention of darkening of latex coagulum where enzymic action is presumably involved. Both methods were used simultaneously in connection with the production of white crepe rubber. However, neither xylyl mercaptan or sodium bisulphite had any noticeable decolorizing effect on guayule rubber although the treatments with these chemicals were necessarily conducted with rubber worms instead of with latex as recommended for Hevea rubber.

Nevertheless, it was demonstrated that treatment of deresinated rubber with acids such as hydrochloric, trichloracetic, or oxalic were moderately effective in reducing color. Rubber treated with strong acid showed poor aging qualities which makes such treatment inadvisable. Oxalic acid may have some possibilities but the problem was not pursued far enough to permit any definite conclusions.

d. Effects of Boiling Treatments. Boiling deresinated worm rubber in water for 30 minutes lowered the molecular weight from 166,500 to 144,700 (Staudinger equation). With ammonia added to the water, the M.W. dropped only to 158,200. The same treatment with resinous worms lowered the molecular weight from 166,500 to 161,000. In the presence of ammonia there was no drop in molecular weight. In boiling whole shrub with or without ammonia present, no significant differences were noted, with respect to the molecular weight of the extracted rubber. However, rubber milled from shrub parboiled in ammonia water yielded a much cleaner rubber on first flotation (before baica) than is ordinarily observed.

5. Recommendations for Future Research.

In factory operation it would be desirable to store shrub during periods when bad weather or other factors prevent the harvest of shrub and its transportation to the factory. The problem of shrub storage needs extensive investigation. In the laboratory this should consist of fundamental studies to determine the exact nature of rubber degradation during shrub storage and the mechanisms which bring it about. Research should then be conducted to determine what, if anything, can be done to inhibit degradation reactions.

If this investigation is successful, then applied research along the lines indicated should be carried out in the pilot plant.

Further work should be done on laboratory scale milling as an aid to pilot plant process development especially for improvement of rubber yields. This constitutes a difficult problem because of the fact that thus far it has not been possible to duplicate the milling action of pilot plant scale equipment in the laboratory. The attritor offers some hope in this direction. A laboratory size attrition mill or refiner, such as manufactured by Sprout Waldron & Co., Inc., which is equipped with different types of plates and a variable speed drive is also suggested for experimentation.

More work is required to determine the effects of chemical additives in the milling liquors. Work to date has indicated, for example, that the addition of a chelating agent will tie up harmful metallic ions. Other chemicals may be found which will improve the color of the rubber, or which will facilitate the milling action. The effect of an antioxidant in the milling medium should also be determined with a view to avoiding possible degradation during milling and subsequent processing.

C. Physical Testing and Compounding Research

The compounding and physical testing section has been concerned with the development of tests, test methods, and equipment which would enable them to evaluate crude guayule rubber in terms of characteristics accepted in the industry as being indicative of quality. In addition, the group has been concerned with methods having high powers of discrimination for evaluating small differences between rubbers, and with the actual evaluation of the rubber produced.

Mooney viscosity determinations, compounding studies, and stress-strain measurements in their various ramifications were investigated and used to advantage.

A large percentage of the time was spent in evaluation for the various units of the laboratory and in control testing of production batches. Detailed records and accounts were kept of all such lots of rubber.

1. Mooney Viscosity Determination

The information obtained with the Mooney viscometer proved to be of greater value with regard to the problems of this laboratory than information from any of the other physical tests performed. These tests have the advantage of being relatively simple to make and of producing the results within a much shorter time than the other methods. The disadvantages are that the results are sensitive to moisture content, resin content, sample preparation, and temperature of test, as well as to the quality of the rubber itself. Methods have been worked out, however, for taking every one of these factors into account for the final interpretation of the results.

a. Sample Preparation. Guayule rubber has a high rate of breakdown. Figure 1 shows breakdown curves for two samples of guayule and one of No. 1

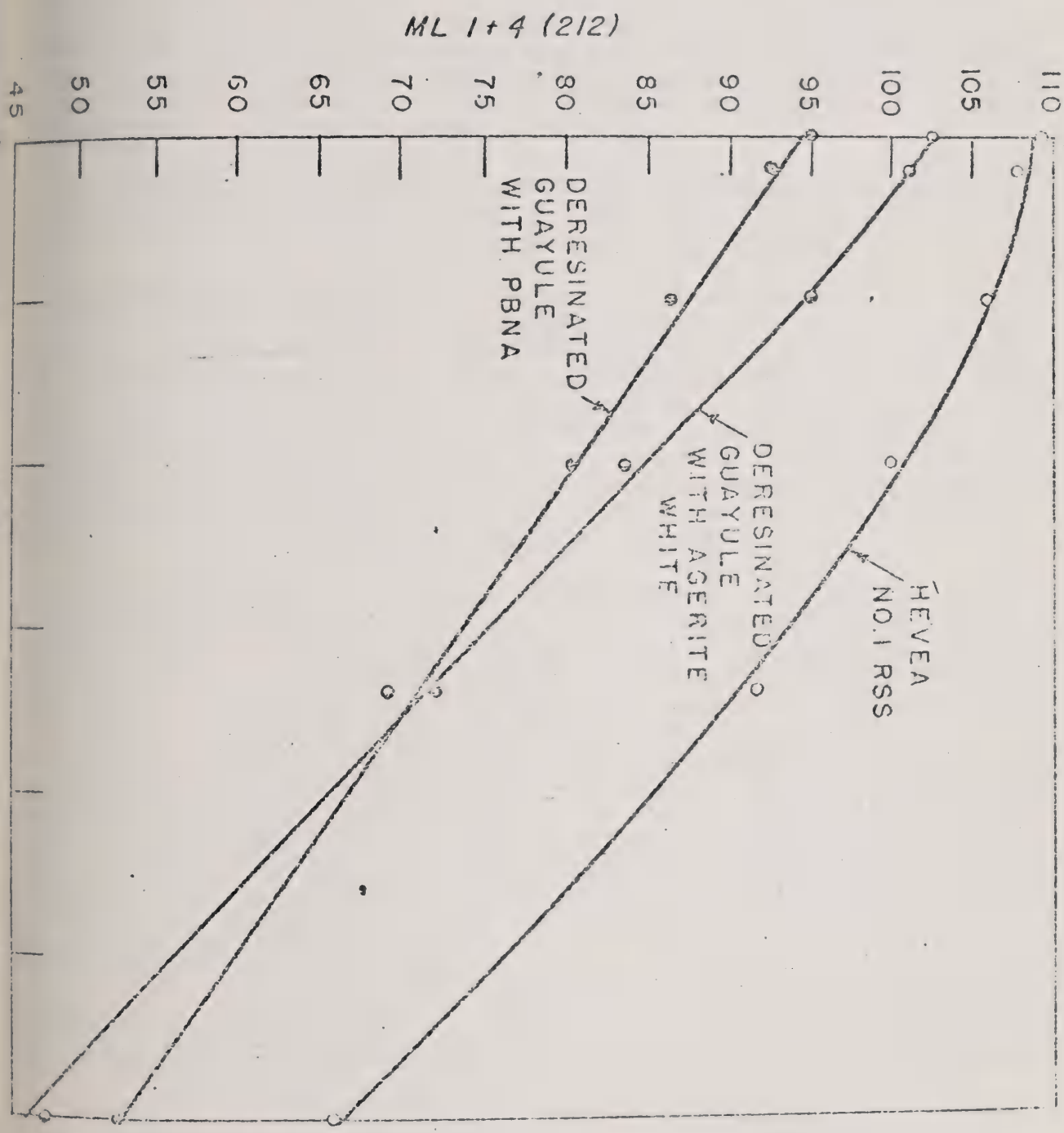

MILL BREAKDOWN
HEVEA
NO.1 RSS
DERESINATED
GUAYULE
WITH ASERITE
WHITE
DERESINATED
GUAYULE
WITH PBNA
ML 1+4 (212)
110
105
100
95
90
85
80
75
70
65
60
55
50
45
0
5
10
15
20
25
30

Figure 1

smoked sheet (Hevea) when mill massed by passing the rubber through a 6 x 12" laboratory rubber mill prior to testing. Because of this fact any method of sample preparation involving a milling procedure lowers the results appreciably and is also apt to produce erratic results. On the other hand, it was discovered that samples tested without milling gave excellently uniform results correlatable with all of the above-mentioned factors except sample preparation. It was further discovered that samples tested as received in worm form or after compressing in a cold Preco press for one minute with approximately 3500 p.s.i. on a 4-inch ram gave the same results. Neither the weight of the sample nor the pressure used were found to be critical for the compressed samples. The usual practice was to adjust the amount of rubber and the pressure used to produce a sheet from which two test disks cut out with a 1-5/8" round die weighed between 25 and 50 grams.

For purposes of this laboratory, the usual practice has been to use the compression method of sample preparation. This was adopted in preference to testing in worm form because of the greater ease of handling.

b. Effect of Moisture. The importance of moisture content in testing the crude guayule rubber had not been fully realized until about the middle of 1952. Since that time it has been the custom to take a 25-gram specimen for moisture determination from the compressed sample described above. The moisture was then determined by a slight modification of the method developed by Max Tryon described elsewhere in this report. Usually the moisture results were available soon after the Mooney viscosity results were obtained. It has been determined that the Mooney value changes approximately 3 units per percent of moisture. The higher the moisture the lower the Mooney value. This relationship is illustrated by the data in Figure 2.

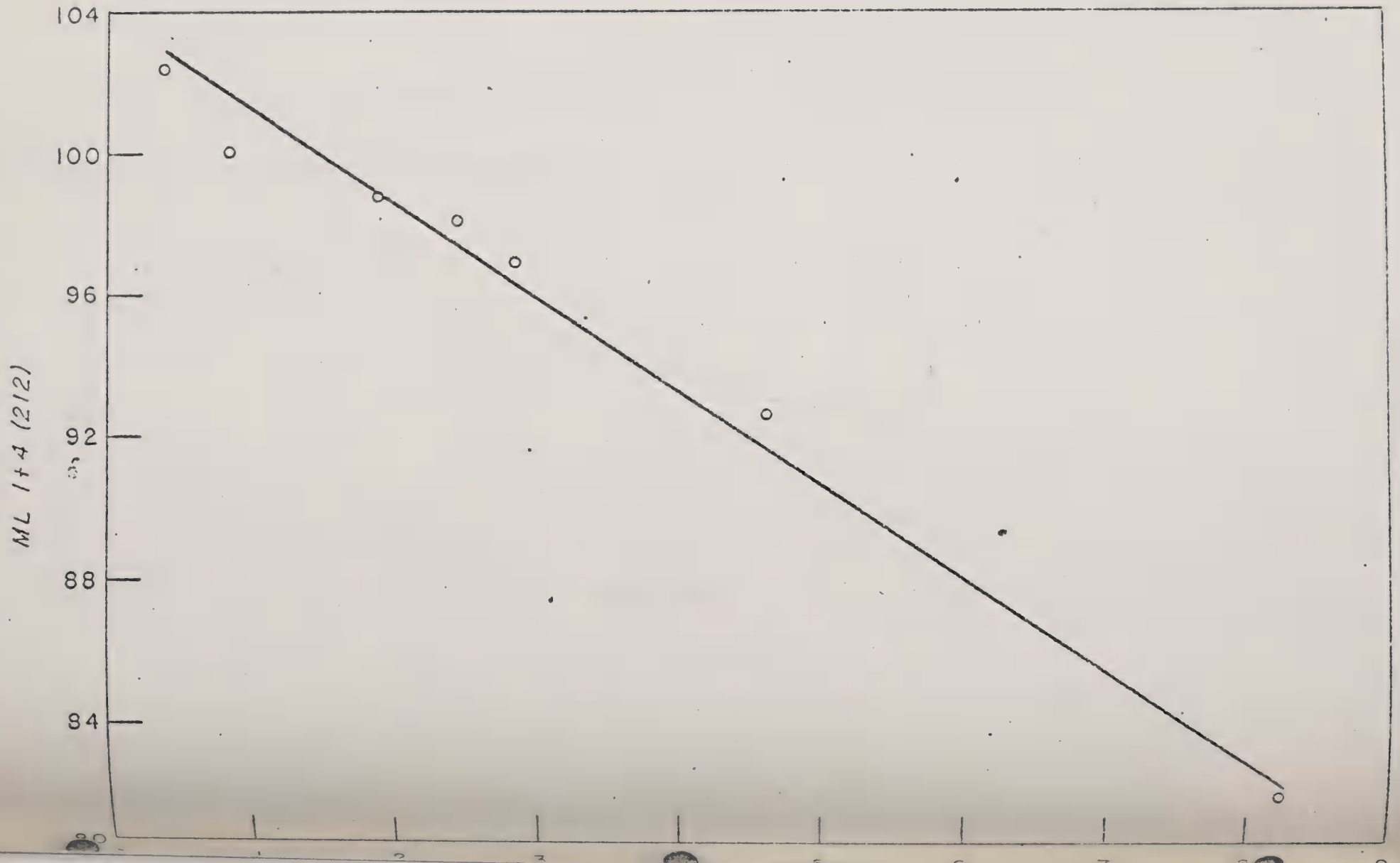
c. Effect of Resin. The resin content (acetone solubles) were determined by the analytical group. A correlation has been determined between resin content and Mooney viscosity, but the validity of the correlation may be open to question since no account was taken of moisture. The work done indicates the Mooney value is changed about 2 units per percent resin, as shown in Figure 3. The moisture contents of the various samples used in this experiment were probably about the same since each sample was treated in exactly the same manner except for the amount of deresination; but there may have been progressively more moisture with higher resin content. It has been observed that rubber containing more resin is more difficult to dry. This work was done before the importance of moisture was realized and no moisture determinations were made. The validity of the results may therefore be in doubt. Nevertheless, resin content does affect the Mooney value---the higher the resin content the lower the Mooney value.

d. Temperature Measurements. Temperature is not a troublesome factor in evaluating crude rubber since methods for controlling it have been well worked out and those recommended by the manufacturer of the instrument are adequate.

In the determination of the curing characteristics, however, temperature becomes extremely important and corrections for temperature variations must usually be made.

The temperature variations which occur in the National Bureau of Standards model viscometer were thoroughly investigated. It was found that the control of the temperature of the test specimen and its measurement in the Mooney viscometer presents a difficult problem, which in all probability will not be solved until the nonsymmetrical characteristics of the machine are corrected

EFFECT OF MOISTURE ON MOONEY VALUES OF GUAYULE RUBBER



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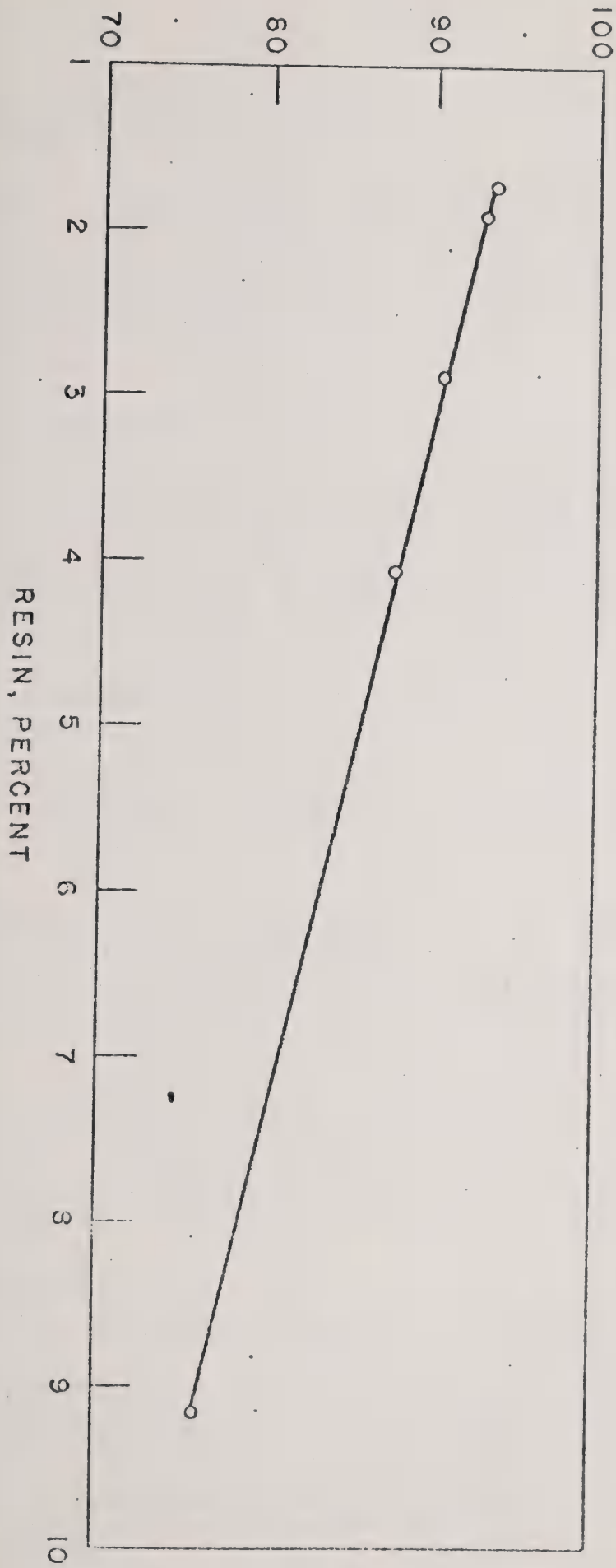


EFFECT OF RESIN ON
MOONEY VALUES OF GUAYULE RUBBER

Figure 3

by a new design. In the meantime, however, some method of indicating the actual temperature of the test specimen as a basis for temperature control must be employed if reliable results are to be obtained.

Measurement of the temperature at specified points in platens, dies, or die holders may be satisfactory for control testing, but it is not adequate for obtaining comparable temperatures from one machine to another for two reasons: (1) the temperature gradients from one machine to another vary widely both in pattern and degree; and (2) the viscosity of the test specimens has a pronounced effect on its temperature curve while thermocouples in the dies are relatively insensitive to the effect.

Thermocouples conforming to the design specified in ASTM Method D1077-49T appear to be satisfactory provided either ASTM Tentative Method D1077-49T or ASTM Ten.M. D927-49T, depending on the test to be made, is followed explicitly. There is no question about the results obtained with an individual machine. There may be some question as to whether or not they will properly indicate the temperature in different machines, since this point has not been definitely determined one way or the other. The fact that the temperatures indicated by these thermocouples at equilibrium agree well with temperatures of the inside surfaces of the dies and that the rate of temperature change with a specimen in the machine agrees with that obtained by means of a thermocouple coiled in the specimen, is strong evidence that the thermocouples may be expected to properly indicate temperatures in different machines.

For precise results in making cure tests with the Mooney viscometer, precise temperature measurements are essential, and if good reproducibility of the viscosity-time curve is required, accurate temperature control is just as important.

c. Interpretation of Mooney Values. In general, interpretation of the Mooney value is made in the following manner. The normally expected value of the rubber is known. The temperature is controlled within the necessary limits, a standard method of sample preparation is used, and moisture content is determined simultaneously with the determination of the Mooney value. Thus the Mooney value may be adjusted to a common moisture level. Therefore, the Mooney value must be a function of the rubber and of its resin content. If the value is normal then it may be postulated that the resin content is high or that there has been deterioration of the rubber during the milling process. Usually a review of the history of the sample will indicate whether or not deterioration has taken place. Thus a fairly accurate analysis of the quality of a sample can be readily made.

2. Compounding Research.

In the final analysis, the only known way of completely evaluating the quality of a rubber is from tests made on cured test specimens and on the final product whatever it may be. There are so many variables introduced into this type of testing, however, that even at best the results obtained are not always conclusive. When it comes to evaluating rubber with small differences such as the difference between one sample of guayule rubber and another produced by some slight alteration in procedure the task becomes almost insurmountable. Nevertheless the effort was made in this laboratory and a measure of success was obtained.

In this type of study the compounding recipe is of paramount importance and one can never say that the recipe which may be right for one rubber is also right for guayule. This is evidenced by the many different recipes used for testing different synthetic rubbers. Once a formula has been selected there are still many factors which affect the results: the equipment used, the compounding and curing procedures, moisture content, temperature variations both in compounding and in curing, the ability of the operator and the precision of the testing techniques.

a. Compounding Recipe. The choice of a compounding recipe depends on the purpose for which the cured rubber is to be used and on the particular type of rubber. In testing it is desirable to use a recipe with good discriminating powers while in the manufacture of rubber products it is desirable to use one which will mask any differences that may exist from one batch of rubber to the next. A good test recipe rather than a manufacturing recipe was required for the work of NREPIP. A considerable amount of progress has been made toward the selection of an optimum recipe but because of the pressure of other work and the limited staff the problem still is unresolved.

Since guayule rubber hydrocarbon is indicated to be identical to that of Hevea it might be expected that a test recipe similar to the ACS recipes used for Hevea would be suitable for guayule. This, however, has not proven to be the case, apparently because of the difference in the constituents other than rubber hydrocarbon in the two types of rubbers. Guayule is deficient in fatty acids even before deresination. Also guayule does not contain proteins as found in the Heveas. On the other hand, the Heveas do not contain the resinous materials found in guayule. Some information is available on the effects of fatty acids and the proteins but very little is known about the effects of the resinous materials on the curing characteristics.

Recipes similar to ACS #2 have given a measure of success with guayule but some further modification is indicated because of the tendency of guayule to act like a stock containing secondary acceleration. That is, the cure is at first delayed and then proceeds rapidly to optimum cure as judged by the maximum tensile value. For test purposes it appears to be the general opinion of rubber technologists that the cure should start off slowly and continue over a long period of time. To date this condition is most nearly met by the following recipe:

Recipe A

100	parts	by	weight	of	rubber
4	"	"	"	"	stearic acid
6	"	"	"	"	zinc oxide
3.5	"	"	"	"	sulphur
1.0	"	"	"	"	Altax

This recipe is the same as ACS #2 except for the substitution of 1.0 part Altax for the 0.5 part Captax found in the ACS #2 recipe. The ACS #1 recipe is the same as the ACS #2 except that in ACS #1 only 0.5 parts Stearic acid is used.

A second recipe was used in conjunction with recipe A above to study the effects of variation in concentration of compounding incredients. Its composition follows:

Recipe B

100 parts by weight of rubber
4 parts by weight of stearic acid
6 parts by weight of zinc oxide
1.5 parts by weight of sulphur
1.0 parts by weight of Altax
.30 parts by weight of TMTD

Variations in stearic acid, zinc oxide, sulphur, Altax (benzothiazyldisulfide) and TMTD (tetramethyl thiuram disulfide) were studied. The effect of adding protein in the form of Bacto Peptone to guayule was also investigated. In general, it appears that 4 parts of stearic acid and 6 parts of zinc oxide are near optimum. The sulphur could perhaps be reduced slightly. Protein improved the properties somewhat but was difficult to disperse. The variability of results in all cases was so great that definite conclusions were difficult to make.

(1) Stearic acid variation. Variation in stearic acid from 2 to 4 parts per hundred parts of rubber were studied in both recipes A and B. The secondary accelerator tetramethyl thiuram disulfide used in B tends to mask the effect of stearic acid. In general, increasing amounts of stearic acid results in longer incipient cure times, probably slower rates of cure, higher tensile and stress values, lower elongation at constant stress values, and less reversion for the longer cure times. Figure 4, elongation at 200 p.s.i. constant stress vs. time of cure at 287°F for the B type recipe clearly demonstrates these characteristics. The lower reversion with higher concentration of stearic acid is even more pronounced for the A type recipe. It appears that because of this fact a minimum of 4 parts stearic acid should be used in any test recipe and it may be that even a higher concentration would be desirable.

(2) Zinc oxide variation. Variations in the concentration of zinc oxide from 1 to 8 parts were studied in both the A and B recipes. In general, results of tests with 2 parts of zinc oxide and less, clearly indicated a deficiency of zinc oxide. Above 2 parts the data were so variable that valid conclusions were difficult to make but 5 or 6 parts appear to be optimum for the type A recipe.

(c) Effect of added protein. The addition of protein in the form of Bacto Peptone definitely improved the physical properties of guayule rubber indicating that the addition of protein to guayule is a factor which might be helpful in producing a rubber which is equivalent to Hevea. The dispersion was so poor and the results so variable that it is not recommended at this time. It may be worth considering for future development.

(4) Effect of variation in sulphur, Altax and TMTD. Some studies were made varying both the concentrations and combination of the above vulcanizers and accelerators. It may be stated unequivocally the higher the concentrations the faster the rate of cure. As to the most advantageous concentrations and combinations for a test recipe, insufficient information is

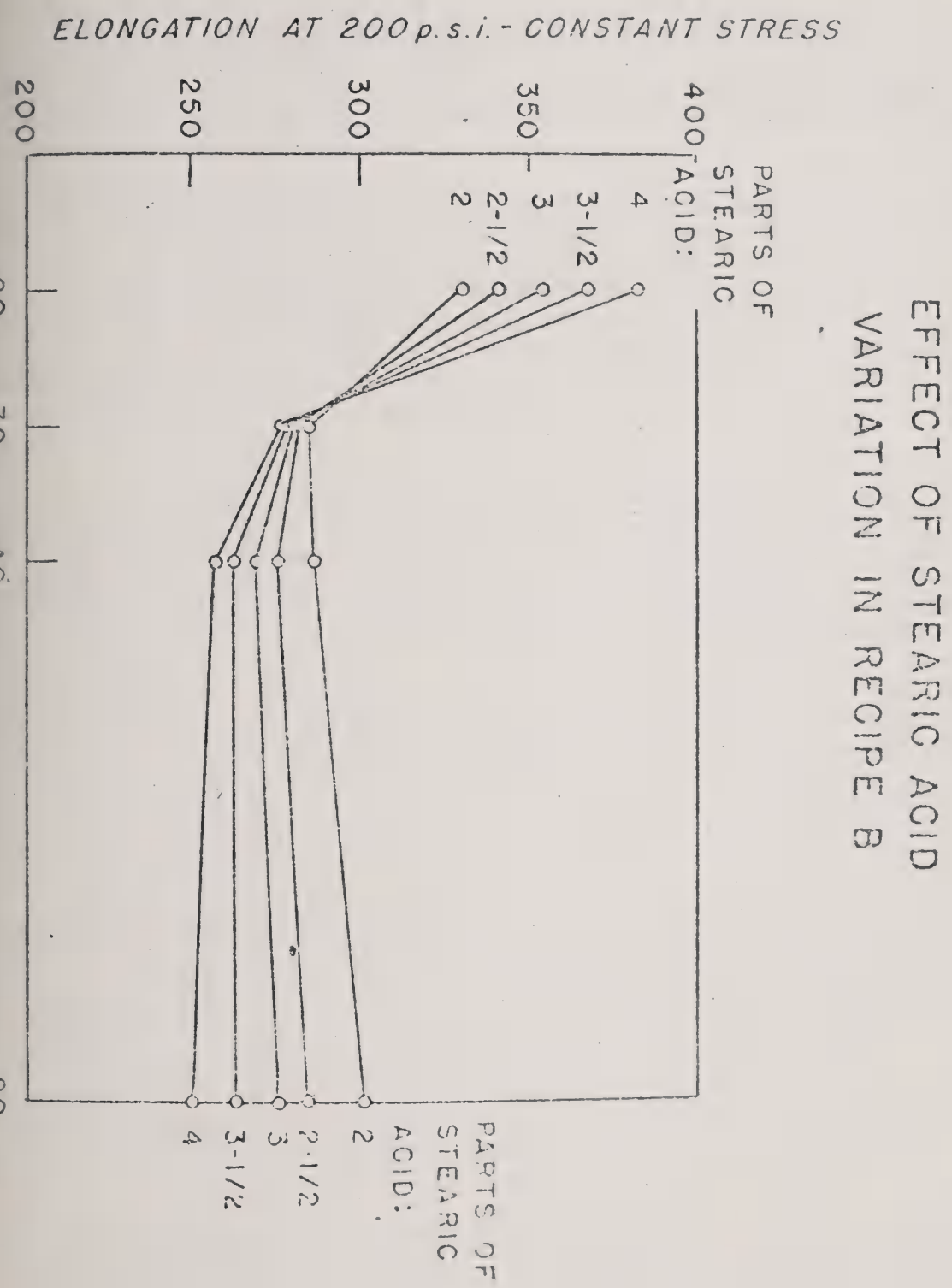

EFFECT OF STEARIC ACID
VARIATION IN RECIPE B
ELONGATION AT 200 p.s.i. - CONSTANT STRESS
PARTS OF STEARIC ACID:
4
3-1/2
3
2-1/2
2
400
350
300
250
200
20
30
40
80
CURE TIME AT 287° F.
PARTS OF STEARIC ACID:
2
2-1/2
3
3-1/2
4

Figure 4

available to permit a definite decision. The best answer that can be given at this time is that both recipe A and B are currently being used. There is some indication but no definite data that the sulphur concentration in recipe A could be reduced.

The data indicated that greater precision both in procedures and of equipment should be obtained before proceeding further to determine the optimum recipe. To some extent this was realized before the compounding studies were started and certain improvements were made. Others have since been made and some are still to be made. A discussion of the recognized factors which affect the results are given below.

b. Effect of Temperature on Rubber Testing. Temperature plays a very important role in the testing of vulcanized rubber. It is important that the vulcanizing press be at a specific temperature for successive cures and just as important that the temperature of the mold cavity be as uniform as practicable. For instance, before improvements were made in the temperature control of the press, measurements of elongation at constant stress on successive test specimens cut from the test sheet were correlatable with relative positions of the specimen in the mold and with the direction of air currents across the press.

Temperature control was improved by installing a Foxboro Dynalog controller recorder with a resistance bulb sensing element in the steam exhaust line, and by shielding the entire press with masonite board. With this set up the average variation was about $\pm$ 0.2°F. and the temperature from the center to the outside of the mold was about 0.4°F. Further improvement is desirable and could undoubtedly be made by having the mold cavity cut into the press platen.

The temperature of the rubber during compounding is also an important factor because of its effect on the rate of breakdown. It is even more difficult to control than the temperature of the press. In general, it can be said that guayule has a more rapid rate of breakdown than Hevea, and that the more the breakdown the lower the modulus and tensile strength and probably the lower the resilience. Thus, it is important to control the temperature of the rubber as well as practicable during compounding.

For comparing one lot of guayule with another, extent of breakdown is not important so long as the relative breakdown is the same in both cases. In comparing guayule with Hevea the amount of breakdown is just as important as the uniformity of breakdown. The effect of mill roll temperature studies indicate that 160°F is just about optimum from the standpoint of amount of breakdown and uniformity of results. At lower temperatures the breakdown was much greater and the uniformity of results poorer. The difference in the results (modulus and tensile) on rubbers compounded at 160°F and 120°F was approximately 8%. At higher temperatures the breakdown was lessened very little and handling of the batch on the mill became increasingly difficult.

The adopted procedure for controlling the temperature of the mill rolls for compounding was to bring the temperature of the rolls slightly above 160°F and then running the mill empty until the temperature of the rolls cooled to 160°F. No cooling water was used. The batch was then compounded without further attention to the temperature. Since all of the rubber tested was of approximately the same viscosity comparable temperatures existed from batch to batch.

The temperature of the rubber at the time of testing also affects the results. Unfortunately, there was no way of accurately controlling or varying the temperature of the testing room. Consequently a definite relationship could not be established. For precise testing the temperature of the testing room must be accurately controlled.

c. Effect of Moisture Content of Rubber. It has long been recognized that the moisture content materially affects the rate of cure of a compounded rubber. Because of the lack of a precise method for measuring moisture content, however, a definite relationship had not been determined. Adaptation of the method recently developed by Tryon for moisture determination has enabled this laboratory to determine this relationship. It has been found that moisture contents of about 1.0% will double the rate of cure, as determined with the Mooney viscometer, over that for a moisture content of about 0.1%. This is illustrated in Figure 5. However, it has been reported elsewhere that the effect of moisture on cure rate is influenced by the pH of the compounded material. Elongation data at constant stress correlate roughly with the Mooney results. Attempts to correlate Mooney results with the parameters calculated from these data failed because of an insufficient number of cures and because cures were not taken at exactly the right times. The National Bureau of Standards has obtained excellent correlation between Mooney results and the parameters calculated from constant stress data. Figure 6 clearly demonstrates, however, the effect of moisture on constant stress. Also, it has an equal effect on the other physical properties.

Undoubtedly one of the greatest sources of error in compounding studies resulted from variation in moisture content. There appear to be two possible solutions to the problem. The ideal one would be a completely and precisely controlled atmosphere in the laboratory. The other would be to determine the effect of moisture for a given recipe and reduce all values to a common moisture level. Either one would undoubtedly improve the quality of results obtained.

The results of the moisture studies are being prepared for publication.

d. Procedures. For reproducibility of results it is necessary to follow a specific procedure in compounding, curing, and to a lesser extent, testing. In the interest of economy the time required should be as short as practicable, but also a sufficient time must be allowed to get proper mixing of the compounding ingredients. Realizing these requirements the following procedure was established for all standard compounding studies:

1. Weigh out the materials for a unit batch containing 300 grams of rubber.

2. Bring the mill rolls to a temperature of 160°F as outlined above.

3. Set the mill opening at 0.015 inch. Place the rubber in the mill and allow it to run for one minute.

4. Open the mill to 0.030 inch without removing the rubber and add the ingredients separately and in the following manner: Add the stearic acid, zinc oxide accelerators and sulphur in that order. Spill each ingredient gradually and evenly across the width of the banded rubber incorporating it as rapidly as possible.

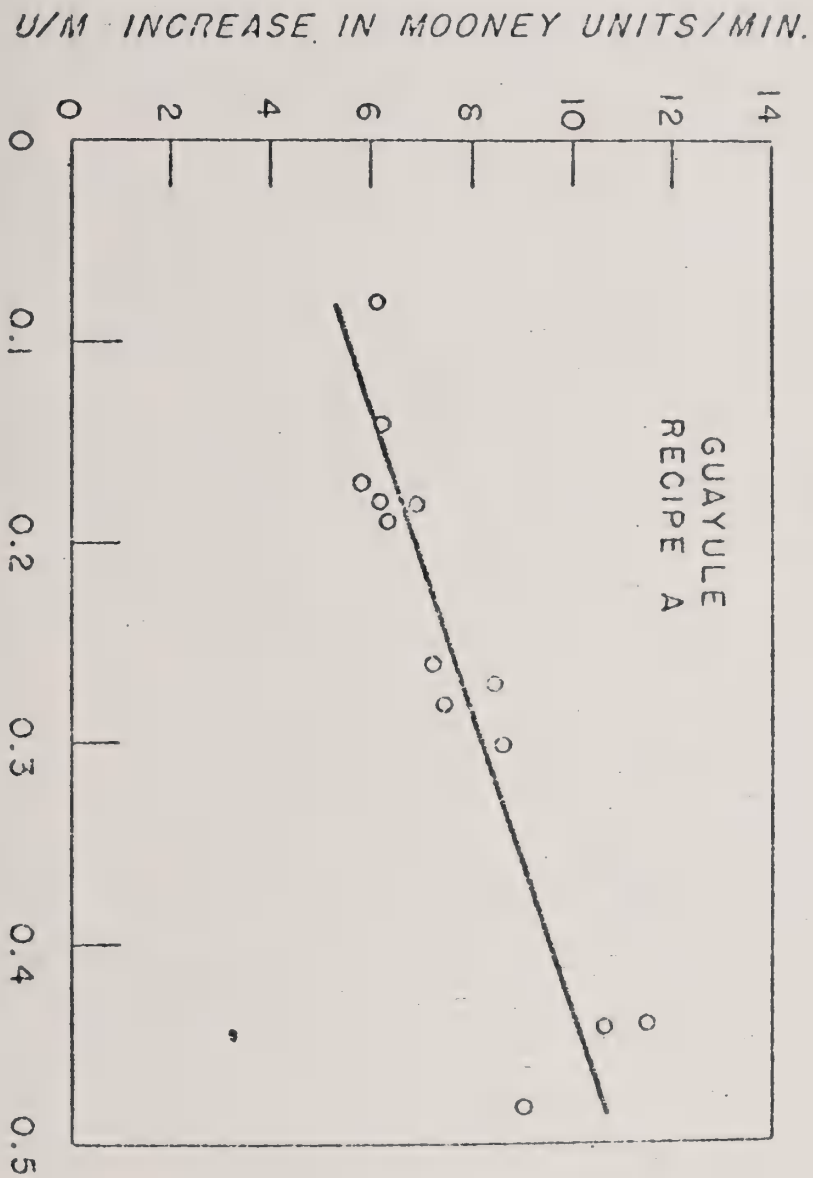

RATE OF CURE
MOONEY UNITS PER MINUTE
GUAYULE
RECIPE A
U/M INCREASE IN MOONEY UNITS/MIN.
0
2
4
6
8
10
12
14
0
0.1
0.2
0.3
0.4
0.5
MOISTURE, PERCENT

Figure 5

EFFECT OF MOISTURE ON CONSTANT STRESS DATA

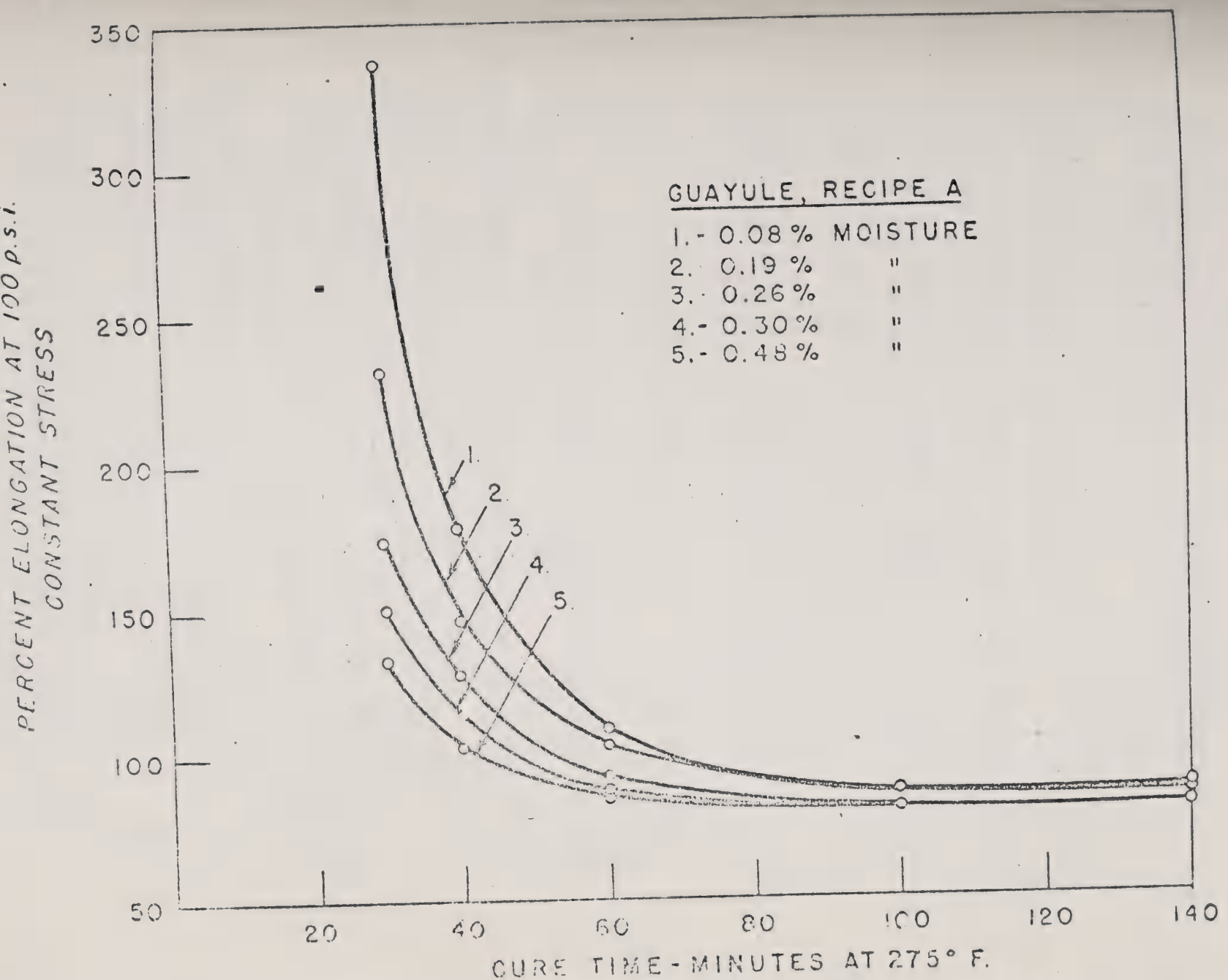


Figure 6

Make two three-fourth cuts one from each side after the addition of each ingredient except sulphur. After the addition of sulphur, make six three-fourth cuts, three from each side.

5. Remove the rubber from the rolls. Close the mill opening to 0.010 inch and pass the rubber through the rolls twice, balling the rubber each time.

6. Open the mill rolls to a setting of 0.090 inch and sheet the rubber off for a 2-hour rest period.

   Adjust the rapidity of operation so that a total time of 10 minutes is required from the time the rubber is first placed in the mill until it is sheeted off for the rest period.

7. Following the 2-hour rest period, refine the compounded stock by passing it six times through the mill with a setting of 0.01-inch and at a roll temperature of 160°F, balling the rubber after each pass.

8. Open the mill rolls to 0.090-inch. Sheet out the stock and let it rest over night before curing.

9. On the day following compounding, cure the stock in a mold conforming to the requirements specified in ASTM D-15 for the preparation of test sheets.

10. Be sure that both the press and the mold are up to the curing temperature before placing the rubber in the mold. Take a sample for moisture determination and for Mooney cure characteristic at the time a sample is taken for the test sheets. Moisture and Mooney determinations should be made simultaneously with press cures. Load the mold quickly, and at the end of the cure remove the test sheets quickly, immersing them in cold water immediately upon removal from the mold. After the sheets have had ample opportunity to cool remove them from the water and dry.

11. On the day following curing, die out test specimens from the test sheets. Measure their thickness, mark and test. Because of the erratic results caused by insolubles it is recommended that 5 tensile and 3 constant stress specimens be used from each test sheet.

c. Equipment. The equipment used in making stress-strain tests of rubber were a 6 x 12" mill, a vulcanizing press, a mold, dies, clicking machine, Scott tensile testers with O.R.R. head, and an M.B.S. strain tester.

The mill used had rolls 6 inches in diameter 12 inches long with guides set 10½ inches apart. The speed of the slow roll was 24 RPM and the friction ratio was 1.4. The mill conformed to requirements of ASTM D-15 on Sample Preparation. The press and mold were described above.

The dies conformed to ASTM D-412 on Tension testing of vulcanized rubber with the addition that special precautions were taken to adjust the width and maintain the dies in a sharp condition.

The specimens width was determined in the following manner:

1. Mark one end of die A the center B and the other end C.

2. Die out one dumbbell from the center of a test sheet and replace the dumbbell in the sheet. Then turn the die 90° to the first cut and die out three more dumbbells in such a manner that the A end of the restricted portion of the die cuts the A end of the restricted portion of the first dumbbell; the B portion of the die cuts B portion of the first dumbbell and the C end of the restricted portion of the die cuts the C end of the restricted portion of the first dumbbell. Label the three resulting square sections A, B and C.

3. Measure the thickness of each section in inches (t) using the regular thickness gage but without the 3-ounce weight. Be sure the gage foot is exactly centered on the square section.

4. Determine the weight in grams of each section in air. (Ra)

5. Determine the weight in grams of each section in distilled water (Rw) to which a pinch of wetting agent (Aquarex D) has been added. With the apparatus available the wetting agent is necessary in order to reduce the surface tension between the water and the suspension wire. Be sure there are no air bubbles adhering to either the specimen or to the under-water portion of the apparatus. Determine all weights to the nearest mg.

6. Determine the temperature of the water and from that the corresponding density (d) in grams/cc

7. Calculate the width (W) as follows:

$$W = \sqrt{\frac{Ra - Rw}{tD} \times .061} \quad \text{inch}$$

Derivation of formula

$$\text{Volume of square section } V = W^2 t = \frac{Ra - Rw \text{ (Wt. of water displaced)}}{D}$$

The factor .061 is required to convert W to inches.

If the specimen width determined in this manner differed from 0.250 inch by more than 0.002 inch in the restricted portion, the die was adjusted and a new width determined.

The dies were maintained in a sharp condition with the aid of special fixtures developed at this laboratory. It has been demonstrated in this laboratory that test specimens cut with perfectly sharp dies will have a tensile strength of about 500 p.s.i. higher than specimens from the same test sheet cut with slightly nicked dies.

The clicking machine used was not entirely satisfactory but gave more uniform results than if a hand mallet had been used in dieing out the specimens. It was an air cylinder mounted on a frame and adapted to the particular use. It was unsatisfactory in that its operation was too slow and that it was not adjustable.

The tensile tester and the strain tester were standard pieces of equipment, carefully calibrated and maintained in the proper working condition. The tensile tester has an inherently large error while the strain tester is quite precise which is the chief reason for using it. The inaccuracies of the tensile tester arise because of the inability of the operator to measure the elongation precisely, to the difficulty of dieing out perfect test specimens, and to the inertia of the pendulum weighing system. A new type electronic head has recently been brought out which would overcome this latter fault. The strain tester has a precision about 10 times that of the tensile tester but tensile strength measurements cannot be made with the strain tester.

D. Conclusions and Recommendations

In testing guayule in a research program where the problem is to produce a better product by improvement of the extraction process, the laboratory is confronted with a much more difficult problem than prevails in the rubber laboratory in general. The precision of testing and attention to details must be immeasurably greater. The conditions must be very carefully controlled and the testing equipment must be the best available. Every factor which is known to affect the results must be carefully weighed and evaluated. Also it is desirable to increase the kinds of tests performed. In addition to those employed in the present program, it would be particularly desirable to perform dynamic tests which would yield information concerning dynamic resilience, modulus, hysteresis, and heat buildup. The high cost of suitable equipment plus the lack of sufficient personnel prevented such studies from being undertaken to date.

In selecting any test or test method, not only the properties measured but the precision of the results attainable should be carefully considered. Naturally the underlying purpose behind a particular experiment will determine which particular methods of evaluation should receive the greatest emphasis, but for general evaluation as many different tests as practicable should be made. These should all have a high degree of precision, should be easily performed, and should be economical both from the standpoint of equipment cost and time consumed commensurate with the information gleaned.

D. Aging and Stability of Guayule Rubber

1. Purpose of Study

Crude guayule rubbers, both resinous and deresinated have relatively poor aging characteristics in relation to high quality Hevea rubbers. The poor aging characteristics of guayule are generally exhibited by severe tackiness. The rubber becomes quite sticky with an accompanying loss in physical properties due to molecular breakdown. This condition has been known to take place in a relatively short time at essentially normal storage conditions.

It therefore became necessary to safeguard the rubber from such degradation if a rubber of maximum quality were to be produced. An investigation was undertaken to determine what factors were responsible for the poor aging characteristics and to find what preventive measures could be taken.

2. Accelerated Aging

a. Apparatus. A means of testing had to be devised whereby the relative aging characteristics of different rubber samples could be studied. An accelerated aging test based on volumetric oxygen-absorption measurements in a specially constructed apparatus was the means adopted. Shelton and Cox have shown advantages for this type of apparatus over other conventional equipment for rubber-aging studies.

The volumetric oxygen-absorption apparatus used was similar to the one described by Shelton and Winn. It consisted essentially of a cylindrical aluminum block drilled with a number of cavities for insertion of test tube-like containers which held the rubber test specimens. The metal block served as a constant temperature bath to maintain any desired temperature for accelerated aging of the rubber. The test specimen containers were connected to a manometric system filled with oxygen and maintained at or near atmospheric pressure.

b. Sample Preparation. It was found that test specimens of crude rubber suitable for oxygen absorption measurements could readily be prepared with the aid of an aluminum mold and a vulcanizing press. The mold consisted of three pieces, each 12 inches square, cut from 20-gage sheet aluminum. One piece had an 8-inch square opening which constituted the mold cavity when placed between the other two pieces. Approximately 35 grams of crude rubber were placed in the cavity, and the mold was held in a laboratory steam-vulcanizing press for 10 minutes at 287°F. (142°C.). This method produced a smooth sheet of uniform thickness, approximating 0.040 inch. In such experiments where test specimens having a thickness in the range of 0.010 to 0.020 inch were desired it was found that the rubber sheet could be more easily prepared without use of the press. In this case a 5-gram sample of rubber was passed twice through closely set rolls of a 4 x 9 inch laboratory compounding mill. Duplicate test specimens were cut from each rubber sheet with the aid of a 1.25 x 3.25 inch template, and weighed.

Antioxidants used in these investigations were milled into the rubber on compounding rolls immediately before the pressing or sheeting step. Milling guayule rubber for as long as 10 minutes had no apparent effect on the rate of oxygen absorption

Crude rubber test specimens cannot be suspended in the oxygen-absorption unit in the same manner as can a vulcanizate. As oxidation proceeds, the crude rubber specimen fails to support its own weight and falls to the bottom of the absorption unit forming a thicker sample. The change in thickness of the specimen causes diffusion limitations which give rise to errors in oxygen-absorption measurements.

Because of these difficulties a method of sample support was devised which was suitable for the aging of crude rubber specimens. This method consists of placing the rubber test specimen between the folds of a stainless steel screen envelope, tieing firmly in place with stainless steel wire and then placing in a vertical position in the oxygen-absorption unit. The screen envelope supports the sample during the aging period and no flow of rubber occurs until late in the autocatalytic stage of oxidation.

These techniques appear to have the following advantages over the test tube film method of sample preparation described by Glazer and coworkers:

1. In evaluating the effects of antioxidants, the content of an added antioxidant is believed to be more precisely known, since the antioxidant is milled directly into the sample which is to be tested. Also, the procedure appears to present a minimum of opportunity for oxidation to take place before the sample is placed under test.

2. No special techniques of sample preparation are required. It is not necessary to use a solvent with the accompanying difficulties of dissolving the rubber, followed by casting and drying a film.

c. Testing Temperature. A testing temperature of 70°C. was used for specimens containing no antioxidants and a temperature of 100°C. was used on specimens containing antioxidants. It does not appear advisible to test specimens at a higher temperature than 100°C. as the volatility of some antioxidants above this temperature may cause errors in the test.

d. Testing Procedure. Volumetric readings on the oxygen absorption apparatus were made periodically to determine the rate of oxygen up-take and cumulative amount of oxygen absorbed by each specimen. The frequency of reading was governed by the stage of oxidation. Readings were made, for example at 8 to 12 hour intervals in the initial period when oxygen absorption was slow. Later, the readings were taken at 2 to 3 hour intervals as the autocatylic stage became apparent.

The crude rubber test specimens were generally allowed to remain under test until one percent of oxygen, based on weight of the rubber, had been absorbed. Deterioration is so pronounced at the level of one percent oxygen absorbed that all rubber-like properties appear to be destroyed and it was not considered worthwhile to continue the test further. The time required to reach this point was therefore selected as the basis for comparing the rate of degradation of differently treated test specimens. However, specimens which were protected by some of the more effective antioxidants failed to absorb one percent of oxygen within a reasonable period of time. In such instances the amount of oxygen absorbed during an arbitrarily chosen period of 200 hours was used for comparative purposes.

3. Effect of Processing Treatments on Aging

a. Resin Removal. One of the most effective processing steps for improving the aging of crude guayule rubber is the removal of resins by acetone extraction. Crude resinous guayule rubber normally contains 20 - 25 percent of resins which can be removed to a minimum of about 1 to 1.5 percent by acetone extraction. These resins apparently contain deleterious substances, because when they are removed from the rubber an improvement in aging is noted.

From the results of aging tests made on rubber specimens containing different amounts of resins, it appears that the more resin that can be removed the better is the aging. However, the improvement in aging is not directly proportional to the amount of resin removed. The first fifty percent removed has less effect on improved characteristics than do the last fifty percent. The effect of progressive deresination on oxygen absorption is illustrated in Figure 7.

b. Chelating Agent. The presence of a chelating agent (sodium salt of ethylenediamine tetra acetic acid) in the milling liquid when guayule rubber is being milled from shrub tissue significantly improves the aging of the rubber. This effect is either due to the sequestering of deleterious metallic ions or to an antioxidant effect in the normal sense.

The metal content (copper, manganese, iron) of rubber milled from shrub which had prior extraction with hot water containing the chelating agent was lower than in rubber produced in the normal fashion. This again indicates that the action of the chelating agent is perhaps a sequestering effect on harmful metals.

c. Stearic Acid. It has been found that the addition of one percent stearic acid to the rubber before the scrub milling operation is an effective means for preventing agglomeration of the raw rubber "worms." Stearic acid also appears to be effective in improving the aging of deresinated guayule rubber. Aging tests performed on rubber with and without stearic acid treatment show a superiority for rubber treated with the stearic acid. The stearic acid is believed to form a protective film about the rubber "worms" which thus shields them against air oxidation.

d. Hydrochloric Acid. One of the processing treatments performed toward improving the color of guayule rubber was the milling of resinous "worms" with hydrochloric acid. Additional treatments were performed using trichloracetic acid and oxalic acid.

Considerable color improvement was attained with the hydrochloric acid as well as a 40 percent reduction in the metal content of the rubber. However, the hydrochloric acid treated rubber had very poor aging characteristics. The hydrochloric acid apparently attached itself to some of the double bonds in the rubber forming a very unstable compound.

e. Milling in Open Containers. When rubber is milled from shrub in an open container (Waring blendor) as opposed to milling in a closed container, a marked difference in aging behavior was observed in the rubbers from the two

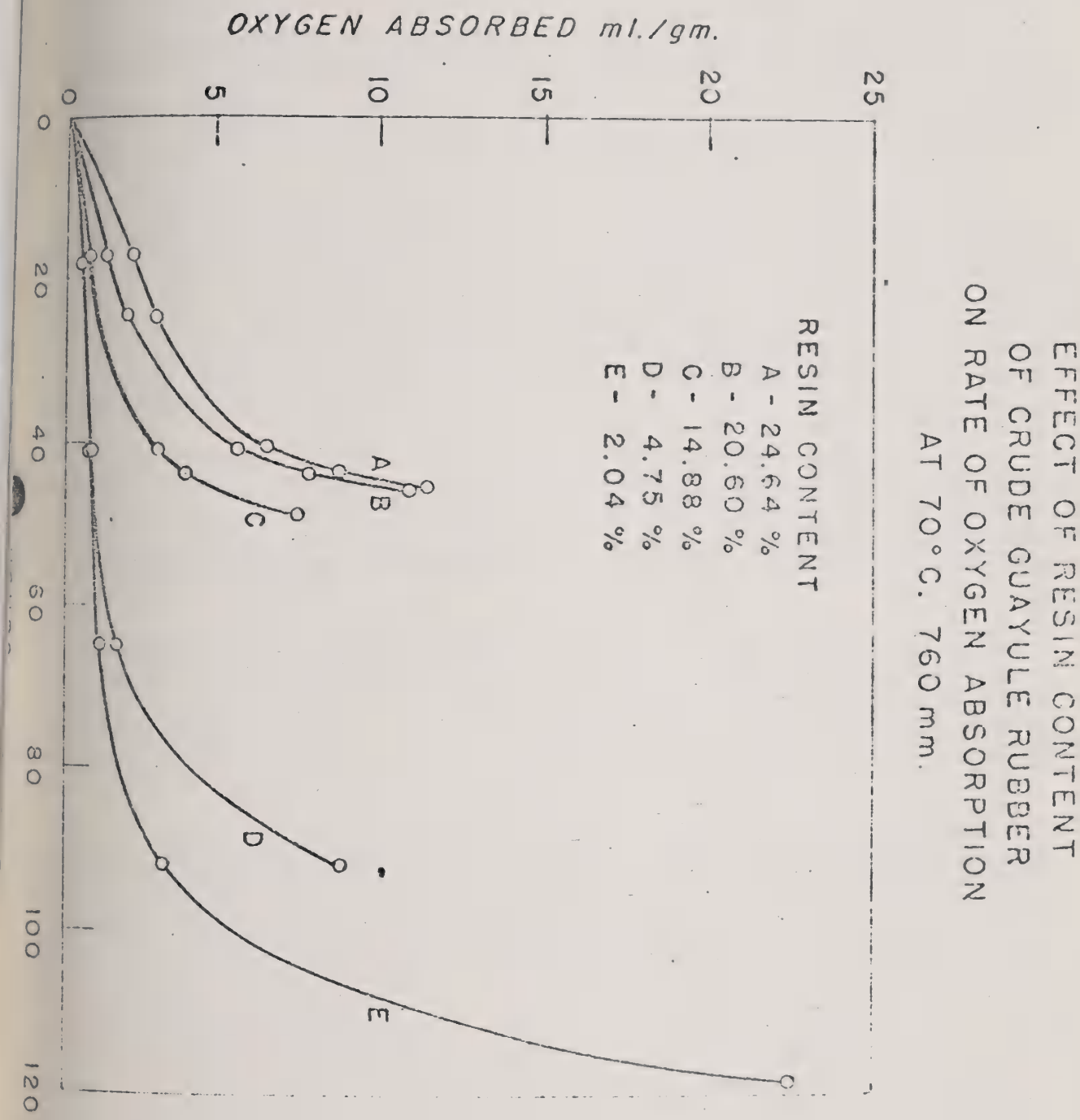

EFFECT OF RESIN CONTENT
OF CRUDE GUAYULE RUBBER
ON RATE OF OXYGEN ABSORPTION
AT 70° C. 760 mm.
RESIN CONTENT
A - 24.64 %
B - 20.60 %
C - 14.88 %
D - 4.75 %
E - 2.04 %
OXYGEN ABSORBED ml./gm.
0
5
10
15
20
25
0
20
40
60
80
100
120
A
B
C
D
E

Figure 7

containers. The rubber produced in the open container had very poor aging characteristics. The apparent reason for this is that the air whipped into the open container started an oxidation chain reaction which consequently led to poor aging characteristics. Observation of this phenomenon was limited to laboratory milling studies.

4. Antioxidant Effects. Crude guayule rubbers, both the resinous and deresinated, do not age as well as does high quality plantation crude rubber. To obtain comparable aging qualities, it becomes necessary to add an antioxidant to the guayule rubber. Accordingly, a study was launched to determine the most effective antioxidant for crude guayule rubber.

a. Effect on Deresinated Rubber. Various chemical antioxidants were milled into crude deresinated guayule at a one percent concentration and then tested in the aging apparatus. Milling or mastication of the rubber does not appear to affect the rate of oxygen-absorption. Among some 26 chemical antioxidants tested, Beta Conidendrol, a by-product of the pulp and paper industry, was found to be the most effective. This same antioxidant was found to be the most effective on GR-S polymers among those tested at the Government testing laboratories at Akron, Ohio.

Alpha Conidendrol was the second most effective antioxidant, Oxynone (2,4 diaminodiphenylamine) the third and Agerite White (Di-beta Naphthyl-para-phenylene diamine) the fourth. Because of its negligible effect on the rate of cure, the antioxidant Agerite White was judged the best all-round antioxidant and was selected to be incorporated in the rubber produced at this Station for industrial evaluation.

Phenolic type antioxidants also appear to be effective protection for crude deresinated guayule rubber. The antioxidant phenyl-beta-naphthylamine formerly used as an antioxidant on deresinated guayule was found to be the eighteenth most effective among the 26 antioxidants tested. The antioxidants were evaluated on the basis of the time required for the rubber to absorb one percent oxygen.

b. Effect on Resinous Rubber. Beta and Alpha Conidendrol were also found to be the most effective antioxidants on crude resinous guayule rubber. However, the best antioxidants for deresinated rubber are not always the best antioxidants for resinous guayule rubber. For example phenyl-beta-napthylamine, just a fair antioxidant on deresinated rubber, is a very good antioxidant for resinous rubber. The reverse is true of the antioxidant, Agerite White.

c. Shelf Aging Tests. The samples of crude deresinated and resinous guayule rubber containing the various antioxidants were submitted to shelf aging tests. These tests were conducted in the subdued light at an average temperature of 70°C. and 45 percent relative humidity. Due to the termination of the project, it was not possible to complete these tests. However, at the end of 14 months no visible deterioration could be found in any of the deresinated samples including the control which contained no antioxidant. For the resinous rubber samples, the control sample containing no antioxidant showed some deterioration. This fact again points to the superiority of deresinated rubber in aging characteristics.

d. Oven Aging Tests. Deresinated crude rubber specimens containing one percent of the antioxidants Beta Conidendrol, Agerite White, PBNA, and a control containing no antioxidant were submitted to oven aging tests. Mooney viscosity readings were determined on these samples after 0, 4, 8 and 24 hours in a circulating air oven at 100°C. The antioxidants were evaluated by this test as follows: (1) Agerite White, (2) Beta Conidendrol, (3) PBNA, (4) Control. These results show very good correlation with the oxygen-absorption results.

e. Influence of Sunlight. Some antioxidants accelerate the degradation of crude deresinated guayule rubber when the rubber is exposed to sunlight. The chief offender in this regard is the antioxidant PBNA. Rubber containing this antioxidant when exposed to sunlight ages more rapidly than the control sample containing no antioxidant. This type of aging is manifested by tackiness and discoloration. Rubber containing the antioxidant Agerite White undergoes minimum degradation when exposed to sunlight.

f. Mooney Viscosity Measurements. The Mooney Viscosity of crude guayule rubber appears to be effected by the addition of certain antioxidants. The antioxidants are usually added to the raw rubber by means of an acetone solution at the end of the deresination process. The addition of the antioxidant PBNA appears to lower the Mooney Viscosity of the crude rubber 2 - 3 units. The addition of the antioxidants Agerite White or Beta Conidendrol however, raise the Mooney Viscosity of the crude rubber 1 - 1½ units. The action of PBNA in lowering the viscosity is probably that of a plasticizer but may be due to inferior protection during drying.

g. Guayule vs. Hevea. Crude deresinated guayule rubber does not age as well as high quality Hevea rubbers. This is due primarily to the lack of natural occurring antioxidants in the guayule. However, when a chemical antioxidant such as Agerite White is added at a one percent concentration to the guayule, it shows aging characteristics superior to raw Hevea rubbers. These relationships are illustrated by the oxygen absorption curves of Figure 8.

If the natural occurring antioxidant of the crude Hevea rubber is removed by acetone extraction, then the guayule and the Hevea have very similar aging characteristics. This again indicates that the primary difference in aging between the crude guayule and crude Hevea is due to the presence of natural occurring antioxidants in the Hevea. It does not appear likely that the difference in aging characteristics is due to the presence of a greater amount of deleterious materials in the deresinated guayule.

5. Discussion and Recommendations

a. Deresinated Rubber. Crude guayule and crude Hevea rubbers have different rates of oxidation, but show a marked similarity in the slopes of their oxygen-absorption curves. It therefore seems likely that the mechanics involved in the oxidation of the two rubbers must also be similar. Oxygen-absorption curves of the two rubbers show a characteristic constant rate stage followed by a rapid autocatalytic stage. In addition, both rubbers on examination after reaching the autocatalytic stage, show much tackiness indicating chain scission. This is in contrast to the oxidation of synthetic GR-S which shows a hardening or oxygen cross-linking of the rubber molecule in the late oxidation stage.

COMPARISON OF OXYGEN ABSORPTION RATES
OF CRUDE GUAYULE RUBBERS WITH CRUDE HEVEA RUBBERS
AT 100° C. 760 mm.

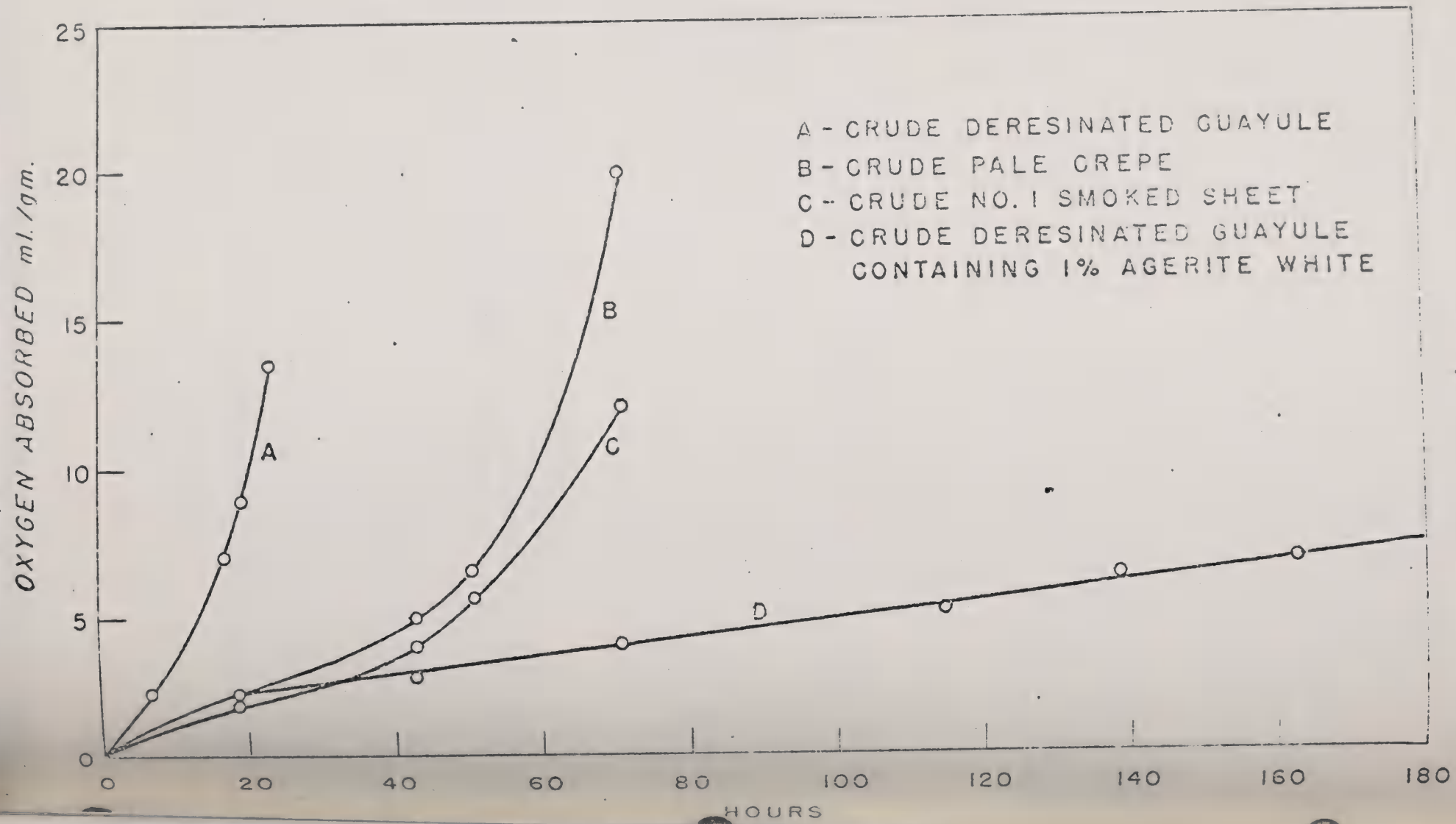


Figure 3

Acetone extracted crude guayule and crude Hevea rubber besides exhibiting similar oxygen-absorption slopes, also have practically idential rates of oxidation. This is believed to be due to the removal of the natural occurring antioxidants from the Hevea, and an increased rate of oxidation. The similar rates of oxidation of acetone extracted crude Hevea and crude guayule indicates that guayule does not contain any more deleterious materials which would influence oxidation than does the Hevea. The poorer aging of the raw deresinated guayule appears to be chiefly due to its lack of natural occurring antioxidants. Therefore to achieve comparable aging between crude deresinated guayule and crude Hevea, it becomes necessary to add a chemical antioxidant to the guayule. When this is done, the guayule shows superior aging characteristics when tested by oxygen-absorption measurements. However, it remains to be determined whether or not the use of Age Rite White or some other antioxidant will provide adequate protection over a prolonged period of time under various conditions of storage.

b. Resinous Rubber. The influence of resin in lowering the aging resistance of guayule rubber has been well established. However, the mechanism by which this increased rate of oxidation occurs, is not clearly known. During the course of oxidation of rubber, peroxides are formed, which in turn react with oxygen and rubber forming more peroxides until finally the autocatalytic stage of oxidation is reached. One factor considered responsible for the rapid rate of oxidation of resinous rubber was the possible presence of unstable peroxides in the resin. With this in mind, rubber samples containing various fractions of resin were analyzed for their peroxide content. Although a small amount of peroxide was found in each sample, including the deresinated sample, no significant difference in amounts of existing peroxides could be found among the different fractions. This indicates that initially no more peroxides occur in any one fraction of resin than another.

It therefore seems possible that if the peroxides are not present initially, then they are likely formed during aging by the decomposition of peroxidizable substances contained in the resin. One of the chief components of guayule resin is the compound linoleic acid which comprises about 50 percent of guayule rubber resin. This compound is readily oxidized by air, light, heat, moisture, and certain metals. It is quite possible that linoleic acid is one of the compounds responsible for the rapid degradation of resinous guayule rubber. If peroxides were formed during the oxidation of linoleic acid, they could readily react with the rubber, thus accelerating its rate of oxidation.

Rubber solutions containing various amounts of resins, which included linoleic acid, were analyzed for peroxides. No significant build-up of peroxides was observed over a period of two weeks. These solutions were exposed to ordinary laboratory diffused light over this period with the exception of 30 minutes exposure to morning sun on one day. Although no viscosity measurements were taken, these solutions appeared to undergo viscosity decreases during the exposure period. Sufficient time was not available to continue this experiment and establish with certainty whether perioxides would be formed during the aging period. However, it seems likely that future research along these same lines may lead to some definite conclusions.

One likely experiment toward determining the mechanism involved in the oxidation of resinous rubber would be the addition of linoleic acid by itself to raw deresinated guayule rubber. By following peroxide build-up and also the rate of oxidation as influenced by linolenic acid, results of significant value could possibly be achieved.

E. Resin Characterization

1. General Description.

The quantity and composition of the acetone extractives vary depending on whether the source is comminuted shrub or resinous worms. Approximately twice as much resin obtains from the first source as compared with the second; however, current deresination practice favors worm deresination because of various operational advantages. Accordingly, a study of the composition of resin derived from the latter source has received particular emphasis, primarily from the standpoint of quality improvement of the rubber but also with a view toward possible byproduct application.

A detailed account of this work presumes a knowledge of several terms coined here for specific use with these materials. Acetone extractives of defoliated comminuted shrub will be referred to hereafter in this report as "shrub resin"; extractives from resinous rubber, ordinarily in the form of worms will be termed "worm resin." The readily emulsifiable acetone-soluble substances, present in low concentration in the aqueous effluents of the pebble milling process, will be termed "effluent resin."

a. Shrub Resin. Shrub resin, essentially a total extractive, is a greenish black, semi-solid mass of complex composition. Heavier than water in density, it is not completely soluble in any of the solvents tried although it approaches complete solubility in acetone, 95% ethanol or dioxane. Moreover, it can be partitioned by means of solvents such as petroleum ether or alcohol into various fractions differing widely in physical and chemical properties. Judging from saponification number and molecular weight determination (cryoscopic in benzene or dioxane) rather high molecular weight (500-1000) unsaturated esters comprise at least half of the shrub resin. The most interesting fraction readily obtainable from shrub resin by solvent manipulations is a hexane insoluble, alcohol-soluble "shellac-like" gum resin. This substance can be easily polymerized to a heat resistant clear coating of good solvent resistance.

b. Worm Resin. Worm resin, on the other hand, is not a total extractive but comprises chiefly the non-polar constituents including most of the polyisoprenoids. The more polar "gum-resins", including most of the aforementioned "shellac-like" fraction, remain with the bagasse by virtue of a greater affinity for wood rather than for rubber. The virtual absence of this fraction imparts a decidedly fluid character to the worm resin which at room temperature or slightly above (30 to 40°C) can be handled readily as a viscous oil. The high refractive index of worm resin (n_D^{20} 1.503) stems more from unsaturation than aromaticity (cinnamic acid being the only aromatic compound known to be present). Worm resin is completely soluble in diethyl ether and dioxane; largely soluble (~90%) in benzene, chloroform, carbon tetrachloride or acetone; moderately soluble (90%) in pentane or hexane; and less soluble (50%) in methanol or 95% ethanol. Useful solvent fractionations have attended the use of pentane (Skellysolve A) particularly.

The process whereby worm resin is obtained has been described in detail in the section on deresination. Wet resinous worms containing 20 to 25% of resin (MFB) on countercurrent extraction with 95% acetone yielded deresinated worms having 1 to 5% of residual resin and an acetone-water miscella containing about 3 to 5% of resin and 30 to 40% of water, depending on operating conditions. The residue after distillation is a greenish-black viscous oil which, after several hours standing, floats on the accompanying water emulsion. The emulsion (6% in resin) can be broken by acidification with dilute mineral acids to yield a resin fraction heavier than water. This fraction has not received any separate investigation.

The composition of the effluent, including the effluent resin, has not been a subject of current studies. However, the work of earlier investigators (McRary, Slattery, Walter, Murray) coupled with our own more recent observations justify making certain speculations concerning composition of the effluent solids. Among the water-solubles are the inulin-and pentosan-hydrolytic oligosaccarides, also betaine and perhaps other amino acids, plus a variety of inorganic salts. In addition to these classes, there is some rubber hydrocarbon in a low state of aggregation, possibly of low-molecular-weight range. There must also be a fair portion of acetone-solubles present, on the basis of discrepancy of resin material balance for the overall process. Its presence, however, is only inferred; it has not been conclusively demonstrated; nor is anything known concerning its composition.

b. Composition of Worm Resin.

Worm resin is the most conveniently isolable byproduct of current guayule rubber processing operations. Its physical characteristics make it a relatively tractable natural product on which to conduct fundamental studies. Therefore, it has been the "piece-de-resistance" of guayule resin investigations over the years.

a. The volatile essential oil fraction has been found, by means of steam distillation, to constitute about 3 to 5% of the worm resin. Its composition probably parallels closely that reported for guayule essential oil (steam distillation of fresh plants) by Haagen-Smit and Siu, who showed alpha-pinene, 60%; dipentene, 9%; cadinene, 8%; and smaller percentages of sesqui-, di-, tri-, and higher terpenaceous hydrocarbons and alcohols. No further work has been done on the guayule volatile oil in the present program.

b. The non-volatile portion (95 to 98%) of the worm resin has been studied here, particularly with attention directed toward the identification or at least the classification of the principal components. One type of classification based on solubility differences in certain of the common solvents, e.g., petroleum ether, methanol, ethanol, etc., has not only demonstrated the complexity of worm resin but has often provided means for achieving useful separations.

(1) Parthenyl cinnamate. For example, workers here have shown that liquid-liquid extraction of ethanolic resin solutions with petroleum ether gives rise to a petroleum ether phase enriched preferentially with parthenyl cinnamate from which parthenyl cinnamate can be effectively recovered via alcohol crystallization.

(2) Parthenol itself has been shown to be present in shrub resin and worm resin to the extent of at least 2.0% and 2.5% respectively. Presumably, it is all esterified with cinnamic acid although this point awaits verification, since the parthenol yield was determined by steam distillation of the saponified non-volatile fraction. Parthenol, while not a major constituent, is an interesting one for several reasons. Rather easily isolated via either the liquid-liquid extraction of the cinnamate or the steam distillation of the unsaponifiables, it is a member of that class of terpenes known as sesqui-terpene tertiary alcohols. Its unique structure was proved in 1948 by Haagen-Smit and Fong. Apparently indigenous only to guayule, parthenol as a novel organic compound potentially useful as an intermediate in syntheses has one notable structural defect. Its stability is not too good. A type of decomposition probably involving the gradual splitting out of water to form parthenene occurs on lengthy storage even at low temperatures. Such behavior has been reported for other sesqui-terpene tertiary alcohols such as cedrol and ledol. If storage of parthenol is ever contemplated, it could be kept indefinitely as the stable cinnamate; other esters may work as well if they can be prepared. As the free alcohol it will keep reasonably well in a refrigerator. Recrystallization from hexane in the presence of charcoal will greatly improve the purity of aged parthenol.

(3) "Dihydroxy-diterpene." From the non-saponifiable fraction another solid terpenaceous compound has been isolated recently. This compound occurs in the crude parthenol fraction from which it can be isolated: (a) by chromatography of hexane solutions on alumina columns (slower moving than parthenol) or (b) recrystallization from aqueous alcohol or nitromethane. Samples obtained and purified by a combination of these methods have yielded white platelets, m.p. 142-143°C. The designation "dihydroxy-diterpene" is tentative and is used mainly to identify the unknown rather than to describe it. However, the experimentally determined molecular weight of 310 does closely fit the indicated class. The compound differs further from parthenol in other important particulars: (a) gives a purple color changing slowly to deep green in the Liebermann-Burkhard test, whereas parthenol fails to undergo any color change; (b) fails to decolorize aqueous potassium permanganate at room temperature while parthenol readily oxidizes under these conditions; (c) generally crystallizes from solutions in the form of platelets whereas parthenol comes down in fluffy needles. In addition to these observations, the unknown failed to form a bisulfite addition complex (not a methyl ketone or dione) but did take up considerable bromine from carbon tetrachloride solution, apparently by addition, to yield a non-crystalline bromide. Elementary analysis should be obtained on this compound. Ultimate proof of structure might prove to be a rather challenging problem, but judging from the quantity of this "diterpene" and its ease of isolation in relatively pure form from saponified worm resin, such a study should be given consideration in any future program.

(4) Cinnamic acid occurs in resin as the ester of parthenol from which it can be easily obtained by saponification. It has already been indicated (see section on parthenyl cinnamate) how the parthenyl cinnamate can be isolated from the resin by means of partition with suitable solvents. The acid may also be isolated from worm resin saponifiables. Its solubility in hot water has been used here as a means of extracting the cinnamic acid from the saponifiables. Alexander in 1911 reported the isolation of an acid melting at 119° which he thought belonged to the cinnamic series. Later, Walter also

isolated cinnamic acid which after purification was reported to melt at 133° (the literature value for trans-cinnamic acid). In the course of the current studies, the cinnamic acid isolated has invariably had m.p. 119° even after extensive purification. Despite the anomolous melting point, this guayule-derived cinnamic acid appears to be chromatographically indistinguishable from known samples having m.p. 133°. The comparisons were handled by micro technique on Whatman No. 1 paper; developing solvent was prepared according to Fewster and Hall; bromphenol blue was used for chromogenic spray. Cinnamic acid showed R_f values of 0.48-0.50 which checked well with Fewster and Hall. No evidence of cis-isomer was obtained by this partition, hence the low melting point of guayule trans-cinnamic acid remains inexplicable at present.

c. The fatty acid fraction constitutes a large (40 to 45%) and consequently important portion of the worm resin. The isolation and identification of its constituents has been accomplished recently here. The following fatty acids have now been isolated and shown to constitute approximately the indicated percentages of the worm resin: alpha-linoleic, 37%; palmitic, 4%; stearic 1.6%; linolenic, 0.5%; oleic, trace indicated.

In general, the procedure for obtaining these acids involves saponifying the resin with an alkaline reagent (aqueous caustic soda is suitable). From the saponification reaction product, non-saponified substances are extracted with an organic solvent (ether). The remainder of the saponification reaction product is neutralized with a mineral acid to precipitate the crude fatty acids. The latter are then washed with hot water to remove cinnamic acid and other water-soluble impurities. Dark colored impurities are removed by dissolving the crude material in pentane (Skellysolve A) and treating the solution with active carbon. This step may be repeated with other solvents such as methanol or acetone to remove colorless non-acidic impurities. The purified fatty acids can then be separated into saturated and unsaturated fractions. This is accomplished preferably by fractional crystallization which involves dissolving the fatty acids in an organic solvent such as acetone or hexane and then reducing the temperature of the solution in stages. The saturated acids are less soluble than the unsaturated acids and crystallize out before the latter. Thus the palmitic and stearic acids crystallize in the form of a eutectic mixture containing 72.5 mole percent of palmitic and 27.5 mole percent stearic acid. The linoleic acid crystallizes out essentially as such with small percentages of oleic and linolenic acid as contaminants. The presence of a trace of oleic acid has been inferred from inspection of the physical constants and elementary analysis of the linoleic fraction. Evidence for the presence of linolenic acid will be discussed in a later papagraph.

Final purification of the unsaturated acid fraction was accomplished by cooling the solution, from which the saturated acids had been precipitated, successively to -55° and -75°C. The precipitates obtained in this way were combined and recrystallized from acetone and then from hexane (10% solutions) at -60°C. The data obtained on the purified linoleic acid have been summarized in table 13.

Table 13. Identification of Alpha-Linoleic Acid in Guayule Resin

Property	Alpha-Linoleic Acid	Guayule Unsaturated Acid
Melting point, °C.	-6.5	-8.5
% carbon	77.09	76.5
% hydrogen	11.50	11.4
Density	d_4^{20} 0.9025	d_4^{20} 0.9036
Index of refraction	n_D^{20} 1.4699	n_D^{20} 1.4704
Mol. Wt. (Neut. equiv.)	280.4	281
Iodine No. (Hanus)	181	175
Tetrabromide Melting point, °C.	115.5	114 - 114.5
% Bromine	53.27	53.22
Hydrogenation	stearic acid	stearic acid

The tetrabromide, prepared according to Markley, yielded on repeated recrystallization from benzene, a small portion of a less soluble hexabromide (62.5% Br.) of m.p. 183-184°. The melting point of hexabromostearic acid has been reported as 185.5-186°. This points to the presence of about 1.4% of linolenic acid in the linoleic acid fraction.

The evidences for the identification of palmitic acid and stearic acid in the saturated acid fraction of guayule resin is summarized in Table 14.

Table 14. Identification of a 72.5:27.5 Mole Percent Eutectic of Palmitic and Stearic Acids in Guayule Resin

Property	Eutectic	Guayule Saturated Acid
Melting point, °C.	55	54 - 54.5
% Carbon	75.23	75.4
% Hydrogen	12.63	12.7
Mol. Wt. (Neut. Equiv.)	264.1	269
Iodine No. (Hanus)	0.0	1.1

Attempts to resolve the eutectic by paper partition chromatography have engendered some promise. Encouraging results were obtained by employing an ascending micro-technique with 80% aqueous acetone as mobile solvent on untreated Whatman No. 1 paper with 1% aqueous potassium permanganate for developer. The use of a stearato chromic chloride or a methyltrichlorosilane treated paper offered doubtful improvement and increased the difficulty of obtaining a satisfactory stain. In no case was complete separation of these two acids realized. However, with each of the eluting solvents tested including 80% aqueous acetone, 90% aqueous methanol, and n-butanol saturated with ammonia-ammonium carbonate buffer solution, there was a pronounced resemblance of pattern between the known fatty acid eutectic and that isolated from guayule resin. This similarity of chromatographic behavior serves to confirm the other data supporting the identification.

3. Other Components.

a. Wax. The occurrence of a "wax-like substance" on the foliage of guayule was first reported by Walter. This waxy fraction was obtained by acetone extraction of the comminuted leaves and flower stems and constituted some 0.25% of the lush foliage, or about 3 to 4% of the acetone extractive of those parts. It was also obtainable in lower yields from acetone extracts of the whole shrub and from the resinous rubber. He reported the following properties for the recrystallized wax: 80.18% carbon; 13.25% hydrogen; saponification number 74.4; molecular weight (Rast) 597; melting point 76°C.

Some additional investigations have been made of this substance which now appears to be a cuticle wax. A solvent extraction procedure for estimating the quantity of this wax in various anatomical parts of the shrub was developed here. It was shown that guayule wax occurs almost exclusively in the phloem above the crown and in the actively growing parts of the shrub, where it probably protects these tissues from excessive dehydration during periods of moisture stress. Wax was also found in resinous guayule rubber to the extent of at least 0.5%.

It is difficult to ascribe a definite set of physical constants to the wax, since its solubility behavior suggests a mixture, perhaps of homologs; however, one fraction of limited solubility (from leaves), purified by recrystallization three times each from benzene and acetone, had d_4^{76} 0.80 (by Ostwald pycnometer) and d_4^{25} 0.963 (by weight of pressed pellet of known volume). This same purified fraction had the following weight percentage solubilities at 25°C.: acetone 0.00; glacial acetic acid 0.01; diethyl ether 0.10; benzene 0.39.

b. Betaine was first encountered in guayule tissue by Murray and Walter who reported its isolation as the hydrochloride salt. It was shown to be present in the product of every step in the extraction of the rubber including the crude pebble-milled rubber. Apparently it is most abundant in the water soluble fraction of the leaves, the milling effluents and in aqueous emulsions of worm resin.

Additional work done here recently has been directed toward the development of practical means for the isolation of betaine. To that end, a process was devised whereby betaine can be obtained as a phosphate salt from ethanolic

solutions of the upper (non-resinous) aqueous phase which obtains when the acetone extract of comminuted guayule shrub is subjected to evaporation under vacuum. When carried out according to appropriate directions the betaine is isolated in high yield. It may be regenerated from the phosphate salt by ion exchange methods.

c. Acetone Soluble Rubber. Hot acetone extractives of guayule rubber or guayule plant tissue have been found invariably to contain a significant proportion of a cis-polyisoprenoid termed here acetone-soluble "rubber." This substance may be characterized by its low-molecular-weight range, 2,000 - 20,000 (Staudinger's equation), solubility in hot acetone, infra red absorption pattern, and the bromine content of its bromination product. The crude fraction, as isolated from the rubber or plant tissue by appropriate extraction procedure, is ordinarily contaminated with the waxy fraction, discussed above, and with plant pigments. Purification and/or fractionation can be effected by dissolution, solution and precipitation and columnar chromatographic methods. The origin and physiological function, if any, of this fraction is unknown at present. However, a knowledge of its presence (ca 3-5%) in the worm resin may be important in planning a practical scheme of resin fractionation.

d. Plant Pigments. Three classes of plant pigments are found in guayule, the chlorophyllins, the carotenoids, and the anthocyanins (and anthoxanthins). The water-insoluble chlorophyllins and carotenoids are contained in particulate form in the cytoplasm of pigmented cells. The water-soluble anthocyanins and anthoxanthins are found primarily in the vacuolar sap, expecially of the leaves and floral parts. Very little research has been directed definitely toward the isolation and identification of the particular components of any of these classes in guayule tissue. However, in the course of the resin identification work these plant pigments have regularly been encountered. Their quantitative removal from various resin fractions has often imposed the greatest single obstacle to the clean-up of these fractions. Whenever flowing columnar chromatography had to be resorted to as with the crude polyterpene fraction (on alumina or magnesia) the carotenes and xanthophylls were separated into definite, readily elutable bands. It was noted that saponification destroyed the green color of the chlorophyll. Accordingly, such a unit process can not be employed where chlorophyll is desired as a byproduct. However, most of the chlorophyll of guayule resides in the leaves which could be processed apart from the worm resin. Since a considerable literature exists on the subject of plant pigment isolation from natural products, no further discussion of the first two classes listed will be offered here.

A separate investigation was undertaken, albeit never completed, to explore the anthoxanthin fraction. Several laboratory experiments were conducted which began with hot ethanol extraction of the floral parts of the plant. These extracts were concentrated and the resulting aqueous supernatant layer filtered. The magnesium ribbon test revealed strong positive evidence for the presence of flavonols in the aqueous layer but not in the water-insoluble resinous layer of such extracts. Attempts to isolate a crystalline flavanol fraction from these aqueous extracts were in every case unsuccessful. However, the failure to accomplish this isolation may be ascribed more to the investigators' unfamiliarity with this branch of chemistry than to any other factor. With more time, later investigators employing some of the

romatographic methods recently reported by Wender and co-workers (Univ. of la.) should have no real difficulty in resolving this fraction.

Despite the inability to actually isolate any crystalline flavonols ring current investigations, some definite progress was made by means of rtition chromatography toward their identification. This was accomplished conducting a series of paper chromatographic comparisons between the guayule avonol fraction and various known flavonols including rutin, quercetin, ercitrin, robinin, quercitagetin and hesperidin methylated chalcone. The veloper solvents included (a) butyl alcohol-acetic acid-water (4-1-5 upper ase), (b) phenol saturated with water, (c) ethyl acetate saturated with water,) chloroform saturated with water. The various migrated spots could be obrved by means of a portable ultraviolet light or could be permanently stained th 1% alcoholic ferric chloride or 1% aqueous potassium permanganate. Of e two papers tested, Whatman No. 1 appeared to offer better resolution than M (Reeve-Angel). In one series of determinations, using the ascending micro romatostrip technique of Rockland and Dunn, evidence was obtained for the obable presence of three distinct flavonols in aqueous alcoholic extracts guayule floral parts. With developer solvent (a) fluorescent spots were served at R_f 0.27, 0.42, 0.50. This eliminated further consideration of ercitrin and hesperidin methylated chalcone.

Another set of determinations was made by the descending method with rge strips, again using developer solvent (a). One strip was spotted with microdrops of guayule floral extract, another with 6 drops of 1% alcoholic tin solution, and a third with 2 drops of rutin and 5 drops of guayule lutions. After 17 hours (solvent travel - 13 inches) the strips were removed, ied, and viewed under ultraviolet light. Guayule extract showed spots of e following R_f values: 0.12 (faint fluorescence); 0.27 (dark fluorescence--ained green with ferric chloride); 0.42 (dark fluorescence - stained with rric chloride); 0.48 (light fluorescence - not stained); 0.59 (light fluorscence--not stained). Rutin showed only one spot (0.37) of orange-brown fluorscence which stained green with ferric chloride. The mixture of rutin and ayule showed all spots characteristic of guayule but no spot at R_f 0.37. wever, rutin may be present in guayule floral extract but in the presence the other flavonols shifted somewhat, probably to the 0.42 position. The pot of R_f 0.27 could be xanthorhamnin. Further work will be necessary to nfirm this hypothesis and to definitely identify these pigments.

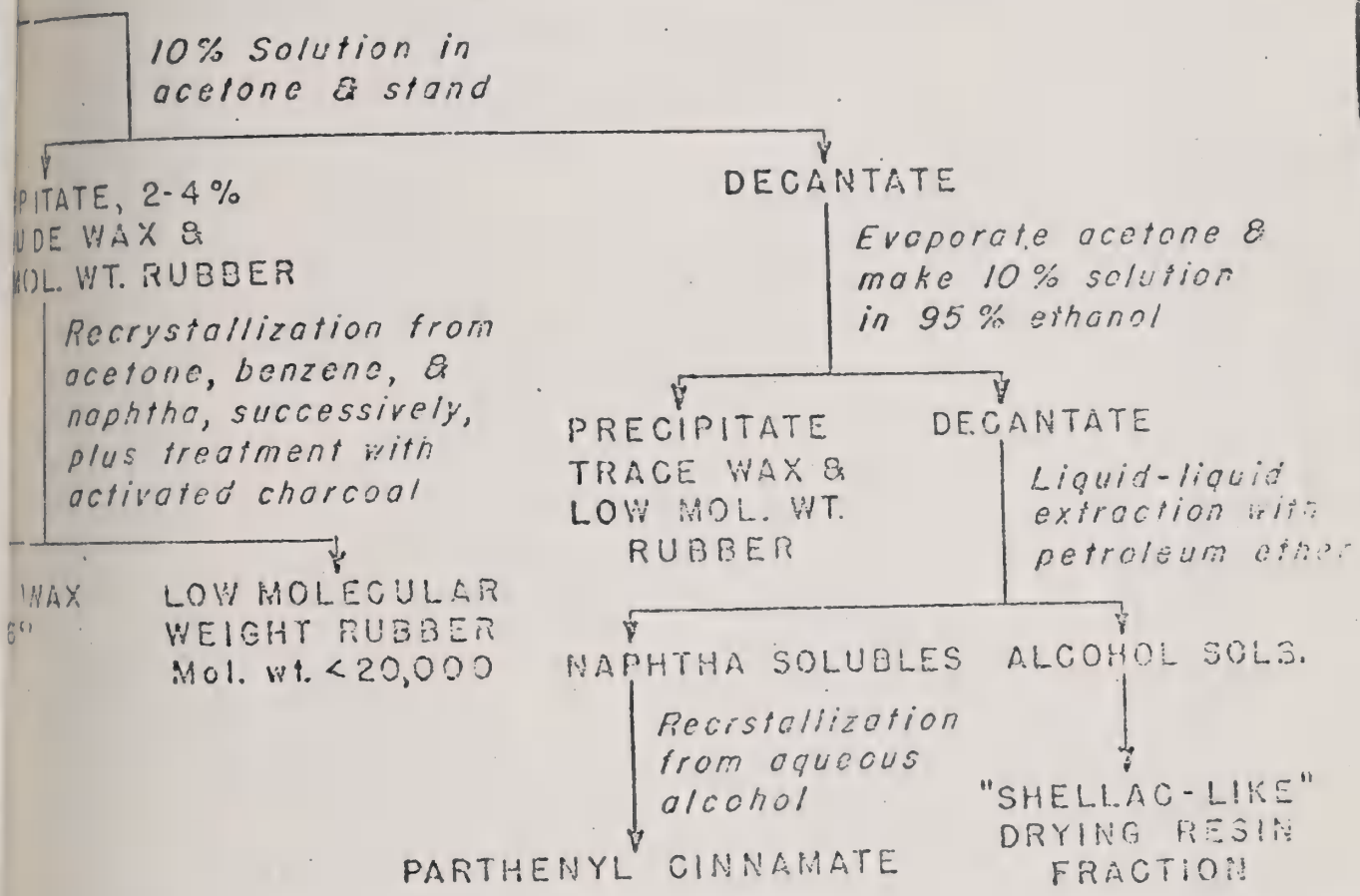
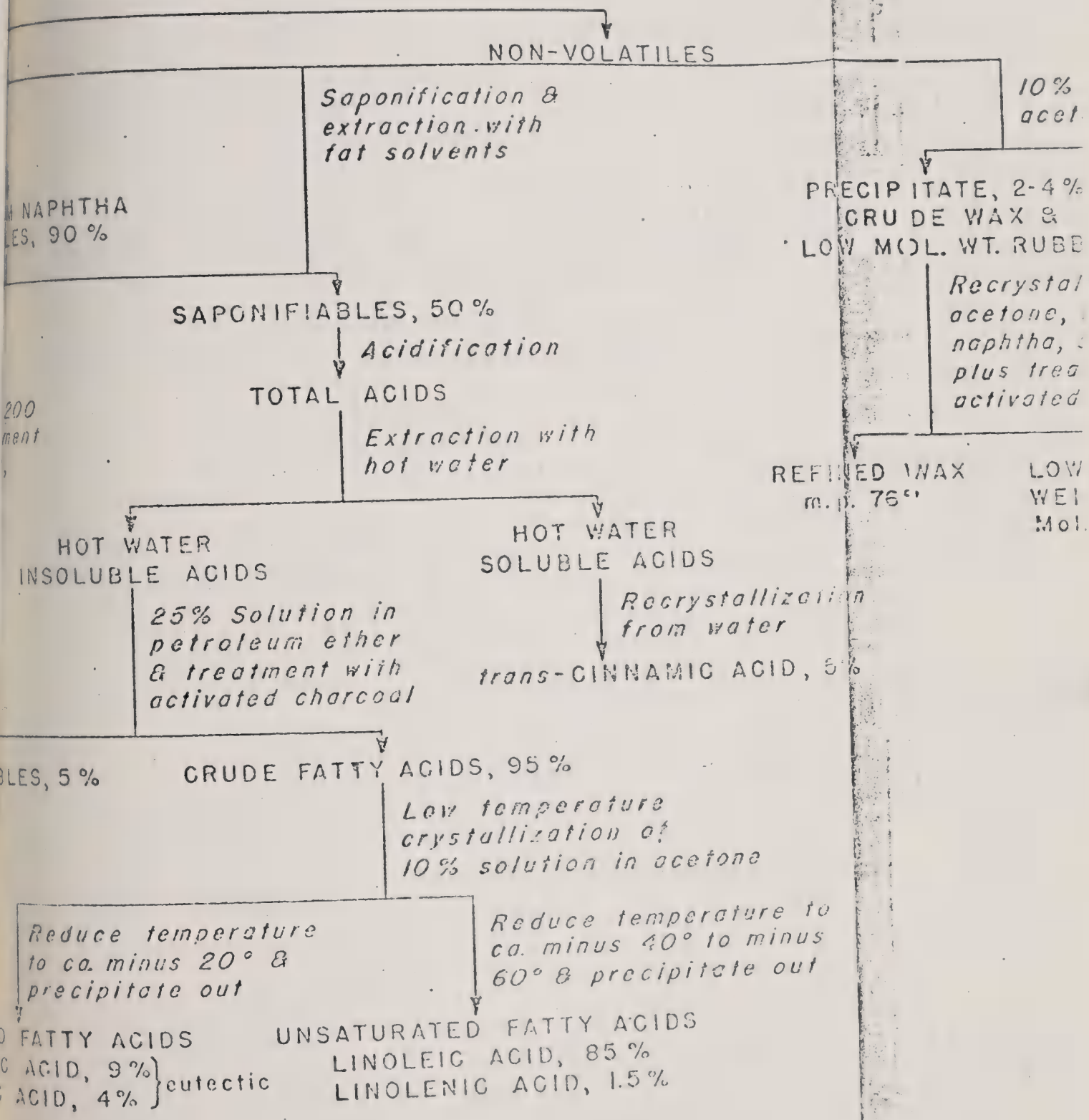

10% Solution in acetone & stand
PITATE, 2-4%
DE WAX &
OL. WT. RUBBER
Recrystallization from acetone, benzene, & naphtha, successively, plus treatment with activated charcoal
WAX
LOW MOLECULAR WEIGHT RUBBER
Mol. wt. < 20,000
DECANTATE
Evaporate acetone & make 10% solution in 95% ethanol
PRECIPITATE
TRACE WAX & LOW MOL. WT. RUBBER
DECANTATE
Liquid-liquid extraction with petroleum ether
NAPHTHA SOLUBLES
ALCOHOL SOLS.
Recrstallization from aqueous alcohol
PARTHENYL CINNAMATE
"SHELLAC-LIKE" DRYING RESIN FRACTION

Figure 9

GUAYULE RESIN FROM WORM DERESINATION



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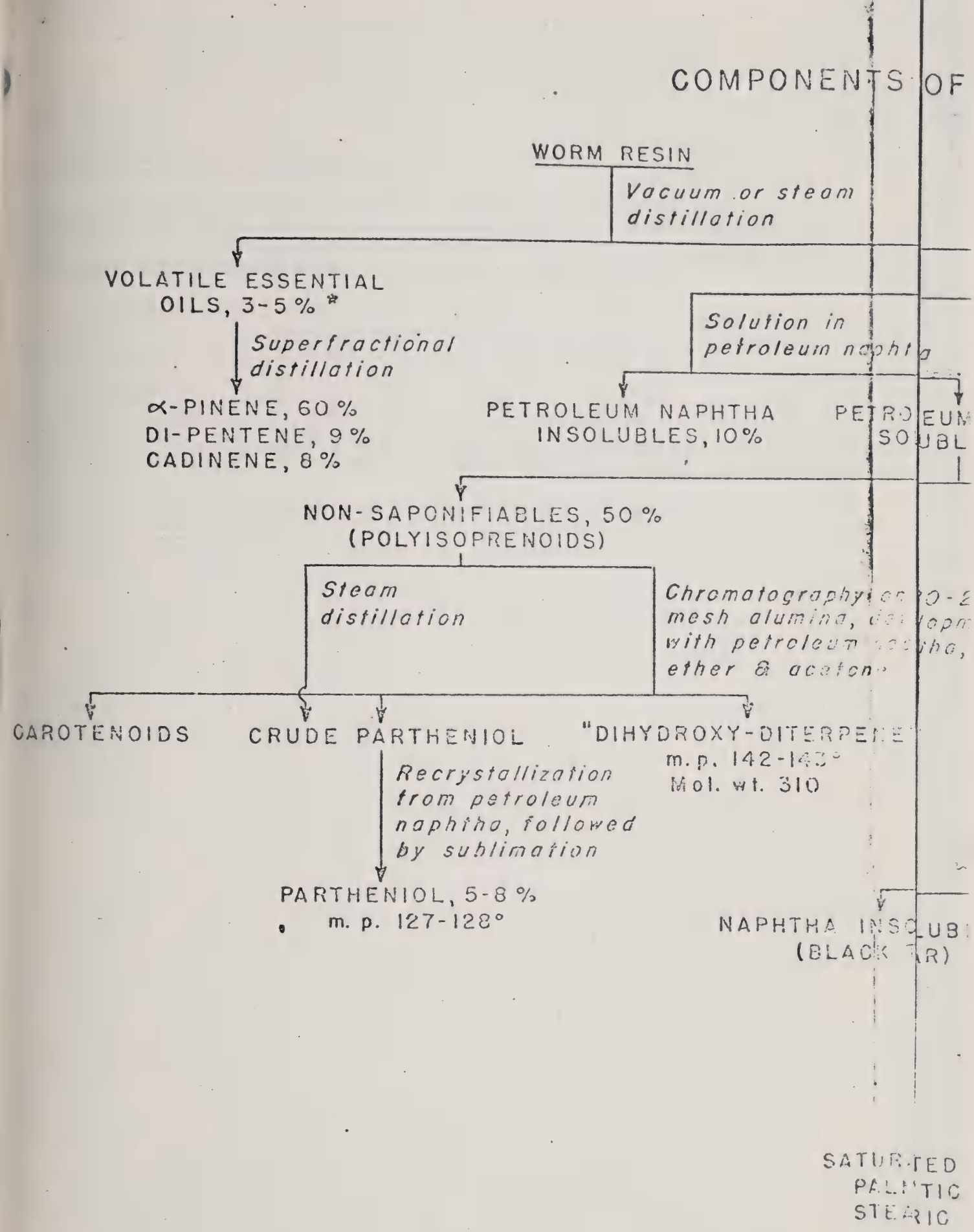

* *Percentages refer to fraction immediately above in all cases.*

Recommendations for Future Work

A sizeable fraction of guayule (worm) resin remaining uncharacterized is the nonvolatile portion of the unsaponifiables. Some progress has been made on this material, but more work of fundamental nature will be required for complete understanding of the composition of this fraction.

Additional work, both fundamental and developmental, should be carried out on the "wax-like substance" to establish its precise structure and to evaluate it as a substitute or extender for carnauba wax.

The "shellac-like" drying resin fraction can be isolated in high proportion from the "shrub resin." If shrub deresination is considered again in the future, this particular resin fraction will be available in such quantity as to warrant inspection of its potential in the paint and varnish industry.

At least three flavonoids have been shown to be present in guayule by paper chromatographic methods. It would seem worthwhile to isolate these compounds and establish their identity.

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SECTION IV

COOPERATIVE RELATIONSHIPS

Index

IV. COOPERATIVE RELATIONSHIPS

A. With Other Government Agencies

1. Bureau of Plant Industry, Soils, and Agricultural Engineering

Cooperative relationships were established between the Bureau of Plant Industry, Soils, and Agricultural Engineering and the Bureau of Agricultural and Industrial Chemistry, at the U. S. Natural Rubber Research Station, for the joint conduct of investigations on domestic sources of rubber -- beginning August 1, 1947 -- under the Strategic and Critical Materials Stock Piling Act. A Memorandum of Understanding delineated the responsibilities and scope of work for each Bureau. Each Bureau undertook work within its usual sphere of activities. The work of BPIS&AE concerned all phases of crop production and genetic investigations. That of the BAIC concerned research on extraction and processing of the rubber.

The BPIS&AE established and maintained all shrub plantings from which harvests were made as required to provide BAIC with the necessary material for extraction process development and related investigations. The millability and quality of rubber of plants of new varieties and hybrids of guayule, selected by BPIS&AE which appeared promising as improved rubber producers, were investigated cooperatively by BAIC.

In addition, there were numerous research problems in which close mutual interest existed and to the solution of which each Bureau contributed valuable assistance, advice or suggestions. Both Bureaus were engaged in molecular weight characterization of the guayule rubber polymer, for example, and much benefit was derived from conferences and exchanges of information on this subject. There was also a joint interest in the use of chemical defoliants for treatment of shrub immediately prior to harvest. Another example concerned the development of new or improvement of existing analytical procedures for the determination of rubber hydrocarbon in plant tissues. Exchange of analytical results on duplicate samples served to increase confidence in methods adopted by each Bureau. A new shaker method of analysis for rubber hydrocarbon, developed by BAIC, was found useful in a special application by BPIS&AE. Joint staff seminars on topics of general interest were held from time to time.

2. Synthetic Rubber Division

The Government Laboratories, University of Akron, Akron, Ohio, which operate under funds provided by the Synthetic Rubber Division (formerly Office of Rubber Reserve), Reconstruction Finance Corporation, Washington, D. C., became interested in the compounding and physical testing of deresinated guayule rubber early in the program. Samples of rubber were prepared at Salinas and submitted for testing by this organization, under the direction of Mr. J. W. Schade.

Later in the program, when it became evident that a superior rubber was being produced from guayule, Mr. Paul S. Greer of the Synthetic Rubber Division made contract arrangements with rubber manufacturers for the con-

struction and testing of heavy-duty truck and passenger car tires in which guayule rubber (produced at the U. S. Natural Rubber Research Station) was used in the carcass stocks in comparison with Hevea (plantation) rubber. Road tests of these tires were conducted by the Government Tire Test Fleet at Camp Bullis, San Antonio, Texas. Detailed reports of both laboratory and tire test results are given under "Laboratory and Related Tests".

3. U. S. Air Force

Arrangements for the construction and testing of airplane tires using deresinated guayule rubber were also aided by the Synthetic Rubber Division in conjunction with efforts of the U. S. Air Force, Wright Development Center, Wright-Patterson Field, Ohio. Mr. K. W. Zahrt and associates, of the Aircraft Laboratory, were especially helpful in planning and arranging for the conduct of the aircraft tire tests. Interest in the possible usefulness of deresinated guayule as a replacement for Hevea, in the event of emergency, was aroused on the basis of results of the Firestone heavy-duty truck tire tests. Contract arrangements were completed with the Frank G. Schenuit Rubber Company, Baltimore, Maryland, for construction and preliminary testing of aircraft tire casings. Further details are reported under "Airplane Tire Tests".

Majors H. E. Mestern and W. F. Barth, and Dr. Stephen Palinchak, of the Air Technical Intelligence, Wright-Patterson Air Force Base, visited Salinas on May 19, 1952 to obtain information concerning special methods for the analysis and testing of rubber vulcanizates. The problem of distinguishing between guayule and kok-saghyz or other rubbers was discussed. After a tour of the BAIC laboratories and pilot plant and the BPISAE facilities, the men were taken to the U. S. Naval Laboratory at Mare Island for further conferences with Mr. Ross E. Morris. A comprehensive treatise recently published in Germany, dealing with Soviet research and developments on natural rubber, was left on loan to BAIC personnel for whatever use it might have in furthering the domestic rubber research program.

4. U. S. Navy

The U. S. Naval Rubber Laboratory located at Mare Island, Vallejo, California, was visited periodically by staff members to consult with Mr. Ross E. Morris and his co-workers on problems of mutual interest. Many helpful suggestions were obtained with respect to the possible usefulness of guayule rubber in defense and other applications. Sample lots of guayule rubber were tested at Mare Island to determine behavior at low temperatures such as are on ships operating in Arctic regions. Further details are reported under "Low Temperature Evaluation". Samples of guayule resin were also provided for an investigation of plasticizers for synthetic rubber for improvement of low temperature characteristics of the latter.

Dr. Peter King, of the U. S. Naval Research Laboratory, Washington, D.C. was consulted regarding the usefulness of infrared spectroscopy for the characterization of rubber and resins. It had previously been shown by Dr. King that purified guayule rubber gave an infrared spectrum essentially identical to that of Hevea rubber. Dr. King offered further cooperation for related characterization studies.

5. National Bureau of Standards

In the Department of Commerce, the Rubber Section of the Division of Organic and Fibrous Materials, National Bureau of Standards, rendered valuable assistance in numerous conferences that were held from time to time with Dr. L. A. Wood, Dr. Norman Bekkedahl, and others of its staff members, notably with respect to the conduct of viscosity measurements, stress-strain and related physical tests on vulcanized rubber, low temperature properties of natural rubber, analysis of crude rubber for rubber hydrocarbon and trace metals content, and other topics.

Cooperative tests on guayule latex, vulcanization characteristics of deresinated rubber, and metals analyses were conducted at the National Bureau of Standards, using samples supplied from Salinas. More detailed results are included under "Laboratory and Related Tests".

6. Texas Agricultural Experiment Station

Dr. S. E. Jones, Vice-Director of the Texas Agricultural Experiment Station at College Station, expressed an interest in the possible utilization of dried guayule leaves for stock feed. The guayule leaves were visualized as a byproduct of rubber extraction operations in the event a guayule rubber industry became established.

Samples of the leaves were shipped from Salinas, and feeding trials were conducted by the Experiment Station. Further details are reported under "Miscellaneous Cooperation".

B. With Foreign Countries

1. Mexico

Guayule rubber has been produced commercially from wild shrub in Mexico beginning about 1902 and continuing more or less continuously, depending upon availability of shrub and price of rubber, until the present time. Although numerous companies have been engaged in producing guayule rubber in Mexico, the only known remaining producer is the Continental Mexican Rubber Company with it's factory at Torreon, Coah., Mexico. This Company is a subsidiary of the Intercontinental Rubber Company with headquarters in New York City.

During the course of the investigations at Salinas, it appeared desirable to make comparisons of quality between the rubber produced at Torreon and that developed as a result of research, particularly with reference to the milling of freshly harvested shrub and deresination.

Arrangements were made in February 1951 by Mr. C. F. Speh, Assistant Chief, RAIC, with Mr. J. H. Linxweiler, President, Intercontinental Co., to ship a sample of freshly milled resinous guayule rubber worms from the Torreon factory to Salinas for deresination. The purpose was to compare the results of analysis and physical tests with those of a deresinated lot prepared at Salinas.

The shrub used at Salinas was 9-year-old variety 593 grown on the Guidotti field. It was parboiled, defoliated, cut and crushed the same day as harvested, and milled the following day.

The sample of resinous rubber worms from Torreon was collected in the wet condition and placed in 5-gallon tins in preparation for shipment. Additional water was added to prevent clumping and deterioration. No information is available concerning the detailed history of the shrub from which this rubber was milled. However, we are informed by Mr. R. D. Ross, Plant Manager, that the rubber was "run of the mill" and that, under present conditions, about 12 to 14 days elapse between the time the shrub is pulled and the time it arrives at the mill for processing. Because of a prolonged drought the shrub had a low moisture content and did not require additional storage to bring the moisture level down sufficiently for milling. The shrub was not parboiled and hence was milled with leaves.

The sample lot of worms, which constituted approximately 25 pounds dry weight, were shipped from Torreon by air express on February 21, 1951. The material was received in excellent condition at Salinas on February 23. It was immediately deresinated by a batch method of extraction, using acetone in the same manner as currently used with rubber produced at Salinas. No difficulty was experienced in dispersing the worms and conducting the extraction, except for the fact that the worms were quite small and some were lost through the screen during the process. Approximately 1 percent of PBNA (phenyl beta naphthylamine) antioxidant was added to the deresinated rubber.

Chemical and physical characteristics of Salinas and Torreon crude rubbers are tabulated in Tables 1 and 2.

In May 1951, Mr. K. W. Taylor, Process Engineer, in company with Mr. C. F. Speh, Assistant Chief of Bureau, visited the factory and environs of the Continental Mexican Rubber Company at Torreon, Coah., Mexico. This visit afforded an opportunity for a broadening of over-all background knowledge of guayule processing. Personnel of the Company including Mr. R. D. Ross, Manager, Mr. Otto von der Heden, Business Manager, and Mr. George Saenz, in charge of field harvest operations, provided every possible courtesy on this trip. Both field gathering of wild shrub, which was conducted at considerable distance from the factory, and factory processing operations were observed in detail.

It was learned that no antioxidant was used for protecting the rubber produced at Torreon. The reason for this was the feeling that the added expense of applying antioxidant was not justifiable in view of the fact that the rubber was being consumed as rapidly as produced. However, Mr. Ross contemplated use of Tonox (p-p'-diamino diphenyl methane) if conditions should justify use of an antioxidant. After a discussion of the shortcomings of Tonox with respect to its effect as an accelerator of cure rate, Mr. Ross requested information concerning use of PBNA, which was then in current use at Salinas. The desired information was subsequently furnished by letter.

Table 1. Comparative Analyses and Physical Properties of Salinas and Torreon Resinous and Deresinated Crude Rubbers

Crude Rubber	Salinas		Torreon	
	Resinous	Deresinated	Resinous	Deresinated
Rubber hydrocarbon, %	75.1	91.9	68.8	90.0
Resin, %	19.8	2.0	25.1	2.0
Insolubles, %	5.6	4.2	6.0	7.1
Ash, %	---	1.27	0.76	0.90
Copper, p.p.m.	---	5.1	10.2	5.4
Manganese, p.p.m.	---	6.2	4.5	4.0
Iron, p.p.m.	---	450	142	185
Mooney viscosity	52	92	41	82
Molecular weight 1/	---	159,100	---	121,400

1/ Values for molecular weight have relative significance only.

These results are largely self-explanatory and show significant differences, particularly with respect to Mooney viscosity and molecular weight in favor of the Salinas deresinated product. Content of insolubles is also lower in the Salinas rubber. However, the content of ash and iron is appreciably less in the Torreon rubber. Differences with respect to copper and manganese are of doubtful interpretation.

Table 2. Results of Stress-Strain Tests of Vulcanizates Prepared from Salinas and Torreon Deresinated Rubbers

	Minutes Cure at 287° F.				
	15	20	30	40	80
SALINAS					
Tensile strength, p.s.i.	3610	3900	3800	3500	3200
Stress @ 500% elongation, p.s.i.	460	560	630	620	610
Stress @ 600% elongation, p.s.i.	940	1180	1340	1350	1280
Ultimate elongation, %	840	800	770	760	740
% Elongation @ 200 p.s.i.	346	282	250	244	245
TORREON					
Tensile strength, p.s.i.	1550	3160	3110	3320	3180
Stress @ 500% elongation, p.s.i.	220	520	700	730	720
Stress @ 600% elongation, p.s.i.	380	970	1360	1420	1410
Ultimate elongation, %	900	830	740	740	750
%Elongation @ 200 p.s.i.	499	327	248	234	224

Formula used:		
	Rubber	100
	Stearic acid	4
	Zinc oxide	4
	Sulphur	1.5
	Altax	1.0
	Tuads	.15

On the basis of the test formula used, it is concluded that the Salinas rubber is faster curing and has a 580 p.s.i. higher tensile strength at the optimum cures than the Torreon rubber. The two rubbers appear to have comparable stresses at given elongations and equivalent cures.

The courtesy of the Intercontinental Rubber Company is greatly appreciated in making possible this comparative study.

The continuance of factory operations in the future was stated to be dependent upon price received for the crude rubber rather than upon availability of wild shrub. Economic uncertainties militated against the installation of improved equipment and methods of processing.

Mr. Ross, Manager of the Torreon factory, visited the U. S. Natural Rubber Research Station at Salinas on two different occasions: in April 1951, and in February 1952. Mr. J. H. Linxweiler, President of the Intercontinental Rubber Company of New York City, accompanied Mr. Ross on the first trip. Considerable interest was shown in the progress being made on guayule processing research, particularly with respect to deresination development.

2. Australia

During World War II a great deal of interest was aroused in the possibility of producing rubber from plants (other than Hevea brasiliensis) which might be grown in Australia. Test sowings of both Russian dandelion (kok-saghyz) and of Mexican guayule (seed presumably obtained from the Emergency Rubber Project) were made under the Commonwealth Scientific and Industrial Research Organization auspices. Although the results with kok-saghyz were disappointing, suitable conditions for cultivation of guayule were established. Several acres of the latter plants were grown to maturity in an irrigated area at Loveday, near Barmera in South Australia, and the rubber content of the shrub was determined by laboratory analysis of samples taken over the whole period of growth until harvest in 1949 at the age of five years.

A decision was reached in Australia to harvest the 5-year-old planting and abandon further research on guayule. In order to obtain as complete a record as possible, Dr. I. W. Wark, Chief of the Division of Industrial Chemistry of the C.S.I.R.O., requested the cooperation of the U. S. Department of Agriculture, through Dr. T. C. Bell, Officer-in-Charge of the Australian Scientific Research Liaison Office in Washington, D. C., in determining the milling yield and quality of the rubber in the Australian shrub. Arrangements were made for the conduct of this work at Salinas. Dr. Bell visited Salinas July 8, 1949, to discuss plans for processing.

Six guayule plants were shipped to San Francisco from Sydney, New South Wales, Australia, via air freight and delivered to Salinas on Sept. 19, 1949. These plants were harvested on June 30 and allowed to dry. A parboiling treatment was given the shrub before shipment. The plants were also sprayed with a saturated solution of benzoic acid to inhibit microbiological activity during shipment.

To provide a basis of comparison in milling, 25 plants of the same age class (5 years) were procured from Spence field and milled as a control. There was a marked difference in the size of the Australian and American plants. Those from Australia averaged 24 inches in height from the first lateral root to the base of the flower stems. The locally grown shrub averaged 17 inches. The average dry weight of the Australian plants was 3.29 pounds; that of the Salinas shrub 0.80 pounds per plant, defoliated dry weight basis.

No unusual difficulties were noted for the Australian shrub during the preparation steps. Crushing was a little slower than was the case with the Spence field material, but this is to be expected with shrub of such a low moisture content (13.2%). In one particular the Australian shrub seemed somewhat different from the American material. The Australian material, during crushing, gave off a pronounced odor of turpentine. Our guayule has a characteristic odor, but it is not so similar to turpentine.

Pebble milling was conducted in 27-inch batch mills according to standard procedure. This was followed by paila treatment for decorking, and by scrub milling. The rubber "worms" from the Australian shrub were very finely divided and of a tan, rather than the usual green, color. This was attributed to the drying treatment given the shrub before processing.

The scrub-milled rubber was spread on drying trays and dried in a Procter and Schwartz through-circulation drier. The dried crude rubbers were sampled for chemical and molecular weight analyses, and the entire amounts weighed for calculation of rubber yields. The rubber remaining after sampling for analyses was submitted for physical testing.

On a defoliated dry weight basis, the Australian shrub was found to have a resin content of 8.99% and a rubber hydrocarbon content of 9.96%. The Spence field shrub had 7.88% resin and 12.7% rubber hydrocarbon.

Assuming that the Australian shrub was planted on a 30" x 30" spacing, and assuming a 100% survival, the rubber hydrocarbon yield would be 2259 pounds per acre as compared to 1077 pounds per acre for Spence field material planted at a 28" x 20" spacing.

The shrub in Spence field was established by transplanting in the spring (February or March) of 1944. The Australian shrub was probably planted in April 1943 or May 1944, according to the available information. The Australian shrub was harvested in mid-winter (June 30, 1949), while the Spence field plants came out of the ground in early autumn. Presumably the yearly rubber increment had reached its peak for Australia, but Spence plants will not reach a similar peak until December or January. Even so, it appears that the Australian plantations will far out-yield those of the Salinas Valley. This, of course, is attributable to the greater size of the plants, rather than to the rubber content.

Chemical analyses of the two crude rubbers are shown in Table 3.

Table 3. Composition of Crude Guayule Rubbers Milled from Australian and California Grown Shrub

Source of Shrub	Rubber Hydrocarbon	Resin	Insolubles	Copper	Iron	Manganese	Molecular Weight
	%	%	%	ppm.	ppm.	ppm.	
Australia	63.17	23.33	6.98	9.2	323	6.2	73,000
Salinas	70.06	23.91	6.37	7.7	235	4.3	118,000

It will be noted that the molecular weight of the rubber hydrocarbon was markedly lower in the case of the rubber from the Australian shrub. This may be interpreted as indicating a rubber of inferior physical properties. Such an interpretation is justified when the physical test data are examined. However, it is probable that these inferior physical properties are not an inherent quality of the rubber, but rather reflect the pre-milling conditioning treatment that had been given the shrub after it was harvested. It has been amply demonstrated that shrub should be milled as soon as possible after harvest to avoid degradation.

The metals content of the rubber from the Australian shrub is higher than that of the locally grown shrub. This is most likely due to the fact that the field soil was found clinging very tenaciously to the basal portion of the plants. A high metals content would be expected to contribute to poor keeping quality of the crude rubber.

Both crude rubbers were compounded on the following formula: Crude rubber, 100 parts; zinc oxide, 5 parts; sulphur, 3.5 parts; stearic acid, 4 parts; and Captax, 1 part. The stocks were vulcanized at 287° F. Results of physical tests are shown in Table 4.

Table 4. Physical Properties of Australian and California Guayule Rubber Vulcanizates

Physical Properties	Australian	Salinas, Calif.
Mooney (L) 212° F. @ 4 minutes	19	45
Tensile @ 20 minutes cure, p.s.i.	1660	2080
Tensile @ 45 minutes cure, p.s.i.	1560	1760
Tensile @ 75 minutes cure, p.s.i.	1340	1440
Modulus @ 500% elongation, 20 minutes cure	150	210
Modulus @ 500% elongation, 45 minutes cure	180	220
Ultimate elongation @ 20 minutes cure, %	940	890
Ultimate elongation @ 45 minutes cure, %	890	870

It is apparent that the rubber from the Australian plants is inferior to that obtained from Spence field plants. Again, this need not be ascribed to an inherent difference in qualities of the two rubbers, but as indicated above, is probably due to degradation resulting from storage and exposure of shrub prior to milling.

3. Great Britain

Dr. R. G. Newton, Rubber Technologist for the British Rubber Producers' Research Association, Welwyn Garden City, Herts, England, visited the U. S. Natural Rubber Research Station at Salinas from Sept. 24 to 27, 1950. The purpose of this visit was to discuss problems of mutual interest pertaining to the quality, testing, analysis, and grading of natural rubber, and to obtain information on guayule research. He expressed a desire to promote cooperation particularly with respect to the exchange of information between his organization and our Laboratory. Dr. Newton had been stationed at Kuala Lumpur for the previous 10 months on loan to the Rubber Research Institute of Malaya, to investigate the problem of producing crude rubber of greater uniformity with grading according to quality.

A round-table conference was held with members of the staff of BPIS&AE as well as with those of BAIC. At this conference, Dr. Newton discussed his work in Malaya and reported on the progress of the research of the Rubber Research Institute of Malaya. The staff of the latter organization was said to comprise about 80, including 18 European workers. Their work embraced cultural, varietal and pathological studies, biochemical investigations pertaining to composition and properties of latex; and studies on quality and testing. Trouble shooting for the plantations is also an important function. An experiment station cooperates with the Institute. Yields of rubber with improved varieties of trees were reported now to be as high as 2,000 pounds per acre per year. However, the latex from these high-yielding trees was said to be unstable, that is, it cannot be marketed in latex form because of coagulation. Average yields of rubber plantations are, of course, much lower.

Interesting information concerning molecular weight was obtained from Dr. Newton. Viscosimetric and osmometric methods were used. Normally, the molecular weight was stated to run from approximately 700,000 to 2,500,000. A fair correlation with the Mooney viscosity was found. Trees which are not regularly tapped yield a latex of very high molecular weight. However, Dr. Newton did not believe there is any advantage in having a high molecular weight in Hevea rubber because the rubber is broken down on the mill in compounding. Apparently rubber so broken down is the same as if it had a low molecular weight to begin with.

Dr. Newton was interested in our methods of rubber hydrocarbon analysis. In the past, rubber hydrocarbon was usually determined by difference. Better methods are required. Our improved bromination method was regarded as being helpful. The rubber producers are very desirous of having a method for determining the rubber content of Hevea seedlings. The rubber content of seedlings has recently been reported as being correlated with the ultimate rubber-producing capacities. Ordinarily it has been necessary to wait about 7 years before a new seedling could be evaluated.

The British Rubber Producers' Research Association conducted an international Mooney viscosity cross-testing program during 1951 and 1952 in connection with its work in furthering the technical classification of plantation rubber. The purpose of this program was to explore the variations

of precision in determining viscosity of crude rubber with different Mooney viscosimeters in different laboratories, and thereby to provide a more reliable basis for standardization of the test.

The Salinas Laboratory was requested to participate as one of three cooperating, and to recommend two other laboratories. The other two selected were the National Bureau of Standards, Washington, D. C., and the B. F. Goodrich Research Center, Brecksville, Ohio. Other cooperating laboratories were selected by the B.R.P.R.A. in England, France, Holland, Indonesia, Malaya, and Saigon to provide a total of 24 different Mooney instruments.

Samples of three different crude Hevea rubbers were submitted at monthly intervals to each participant. The test results were tabulated, analyzed, and reported to the participants by the B.R.P.R.A. A member of the Salinas staff, who served as Chairman of a task force of the ASTM Subcommittee XII on Rubber Processibility, coordinated the efforts of the three U. S. laboratories in this testing program, particularly with respect to offering suggestions for standardization to the B.R.P.R.A. It was concluded that the most likely sources of deviation or error were inadequate temperature control, improper calibration, and improper die closure of the Mooney instrument.

Mr. W. P. Fletcher of the B.R.P.R.A., who directed the program, commented on the results of the Salinas Laboratory that "We are most interested to observe that your instrument is giving the most consistent performance of all those included in the program....."

Dr. Leslie Bateman, Superintendent of Chemical Research of the B.R.P.R.A. visited at Salinas in September 1952. He was interested primarily in the fundamentals of rubber deterioration through oxidation, and in the reactions of sulphur in vulcanization. He is recognized as an international authority in these fields, and held informal seminars with the staff to discuss problems of mutual interest.

4. Turkey

Mr. Sevket Ozberk, a Turkish trainee, spent approximately one year (beginning September 1949) at the U. S. Natural Rubber Research Station in the interests of the Turkish Government to obtain information and training on the production of natural rubber. Arrangements for this tour of duty were made under the auspices of Mr. Cezmi Berktin, Turkish Educational Attache, New York City. Mr. Ozberk's primary interests were in the cultural development of guayule and kok-saghyz, and consequently most of his time was spent with the Bureau of Plant Industry, Soils, and Agricultural Engineering at the Salinas Station. Approximately one month (February-March 1950) was spent with the Bureau of Agricultural and Industrial Chemistry, during which time Mr. Ozberk gained knowledge of the processing of guayule shrub. Mr. Ozberk, in turn, furnished certain information concerning the methods used at the Rubber Experiment Station of Ankara, Turkey. According to a letter received by Mr. Ozberk from Mr. Hikmet Konuralp, who is in charge of the Ankara Station, the following steps are involved in the extraction of rubber from guayule:

"1. Guayule shrub which has been dried in shade is cut less than 10 mm. pieces.

2. Chopped shrubs are crushed by crusher less than 1 mm. thickness.

3. Crushed shrub mixed with water (usually 8 to 10 parts water to 1 part crushed shrub) in a boiling kettle. In the slurry there is sodium hydroxide solution as much as 5% of the crushed shrub.

4. The mixture (slurry) should be boiled through the steam heat for 4 hours without exceeding 100° C.

5. After 4 hours' boiling, leave the slurry to cool 5 to 10 minutes.

6. Agitate the slurry through the high pressure water. By doing this, there will be pebbling, and small pieces of rubber will float on the surface of the water. Then the first skimming is made.

7. Dewater the wet rubber worm through the screen. Pass the dewatered rubber worm through the steam-heated roller and wash the rubber with water when it sticks around the roller. By doing this, saponificated matter in the rubber will be cleaned out.

8. Pass the rubber through 40°C. heated roller for sheeting.

9. Dry the sheeted rubber in drier at 40°C. This crude, resinous rubber contains 75% or 80% isoprene and the rest is resin.

Dry resinous rubber is deresinated with acetone, using an extractor. At the end of this extraction, we get almost 80% rubber and 20% resin.

After deresination, we sheet the deresinated rubber by passing it through a 40°C. heated roller, then dry it in drier around 40°C. until only 1% moisture remains.

All the equipment which has been used in the above-mentioned processing of guayule is designed by the staffs of the Rubber Experiment Station of Ankara, Turkey."

The Electrochemical Construction Company of New York City, which is engaged in the business of designing process equipment installations and procuring equipment for foreign developments, made inquiries for information relative to the installation of a process for extracting rubber from guayule for the benefit of the Turkish interests. Mr. Robert Spitzer, of the company, visited Salinas on August 24, 1949, for a thorough discussion of the problem.

It was learned from Mr. Spitzer that only a few acres of guayule are now under cultivation in Turkey, but additional plantings are contemplated. There were said to be large semi-desert areas adjoining the Mediterranean shore line which are believed suitable for large scale guayule production. It was desired to set up a pilot plant for the purpose of conducting some experimental work on rubber extraction. It appeared that the Turks desire to produce a deresinated rubber, and have carried on some experimental work. Some experimentation with kok-saghyz appears also to be in progress.

Guayule shrub in Turkey was said at the time to be 5 years old and to contain 22.7% rubber. Judging from the dimensions of the single shrub sample furnished Mr. Spitzer, Turkish guayule is considerably larger than that grown under Salinas conditions. Figures supplied by Mr. Spitzer indicated that an acre contained approximately 1500 pounds of rubber. This is comparable to American shrub production.

The Electrochemical Construction Company expected to supply all necessary equipment for the construction of a pilot plant for the processing of an estimated 300 pounds of shrub per day. Alternate procedures for extraction of rubber were envisaged, including the use of a resin and/or a rubber solvent as well as conventional pebble milling.

Mr. Spitzer was shown the various units of processing equipment in our pilot plant and suggestions were made with respect to sizes and other specifications of the parboiler, cutter, hammermill, crusher, pebble mill, etc., that would be required for the Turks. Advice was given against the expenditure of effort on the development of a process for the extraction of rubber by means of a rubber solvent for several reasons: (1) the rubber is very difficult to extract completely; (2) extremely large volumes of solvent must necessarily be used because rubber solutions become viscous when they contain as much as 2% rubber; and (3) the rubber is apt to be degraded as a result of having been dissolved and would likely be suitable only for products such as rubber cements or chemical derivatives.

At that time, the most promising method for deresination appeared to be through resin solvent (acetone) extraction of the cut and crushed shrub prior to pebble milling, and was recommended for investigation in connection with development of the Turkish process.

5. Spain

Dr. Wifredo de Rafols, a graduate agriculturist of the University of Madrid, visited the Salinas Station on two occasions: in January 1951 and again in February 1952. Dr. Rafols spent approximately a year in the United States on a Seagram fellowship investigating various phases of research on byproduct utilization (notably fermentation of inulin) which would be applicable to the production of rubber from kok-saghyz. He also studied some of the physiological factors which influence rubber formation in kok-saghyz at the California Institute of Technology at Pasadena.

During the first visit, the primary interest of Dr. Rafols was the work of BPIS&AE on kok-saghyz culture, genetics, etc. However, analytical

methods for determining rubber hydrocarbon in plant tissue, as developed by us, were also of special interest. Guayule rubber extraction and rubber quality were discussed. The second visit was made for the purpose of obtaining information concerning our methods of rubber extraction, compounding, testing, and analytical procedures. In addition, Dr. Rafols expressed some very helpful ideas about the possibility of investigating molecular weight and related characteristics of the rubber molecule by means of paper chromatography. Suggestions made by Dr. Rafols were followed up in subsequent laboratory work which demonstrated that rubber polymers and synthetic elastomers could be chromatographed.

Messrs. Aurelio Cabra, a chemist, and Jose Luis Ramos, a forestry engineer, visited the Salinas Station in March 1951, as representatives of the Spanish government, to obtain information concerning all phases of guayule culture and processing. Large scale preparation of deresinated rubber for tire tests was in progress at the time and was witnessed by these visitors. Spain was said to be desirous of producing moderate quantities of guayule rubber to supplement their limited importations of Hevea rubber. Mr. Cabra was at one time a visitor at the Northern Regional Research Laboratory to study processes for utilizing agricultural wastes.

Mr. Francisco G. de la Riva, Vice-President of the Del Amo Foundation of Los Angeles, Calif., and head of the Motion Picture Service of the Ministry of Agriculture in Madrid, Spain, visited Salinas in August 1952 for the purpose of taking motion pictures of guayule culture and processing, and to obtain general information.

The Del Amo Foundation is a privately financed organization whose objective is to foster good relationships between Spain and the United States through the exchange of fellowships. Mr. de la Riva stated that he was making a general agricultural film in the United States for educational use in Spain.

Motion pictures were taken by Mr. de la Riva of the buildings and grounds at the Salinas Station, the out-door deresination process, and various other operations including shrub harvest, seed collection, and pollination work of the BPIS&AE. No pictures were taken inside the pilot plant because of poor light conditions.

Mr. de la Riva reported that an experiment in guayule production, comprising several plots totaling approximately 20 acres, was in progress near the southern coast of Spain. The area, which totals several hundred thousand acres, is sandy and until recent years was not considered suitable for agriculture. The Director General of Forestry of Madrid had requested Mr. de la Riva to obtain whatever photographs and information on guayule culture in the U. S. that was possible for assisting in the Spanish experimentation.

It was also learned that a small pilot plant for extracting the guayule rubber had been set up in Spain. It reportedly consists of several tube mills which are smaller than those in use at Salinas. Porcelain balls are used instead of pebbles. The shrub is dried in preparation for milling and

leaves are included in the milling. It appears that some retting has also been attempted, but detailed information on this and other points were apparently not known to Mr. de la Riva.

During early 1953 inquiries were received from Mr. Angel Zalve, a representative of the Governor at Seville, concerning problems that had been encountered in laboratory scale compounding and vulcanization of the crude guayule rubber produced in Spain. Efforts to set up experimental deresination equipment were briefly described. Deterioration of rubber during or following processing appeared to be the principal problem confronting the Spanish workers. Appropriate suggestions and description of methods in use at Salinas were forwarded to Mr. Zalve.

6. France

Dr. Jean Le Bras, Inspector General of the French Rubber Institute and of the Institute of Rubber Research in Indo-China, visited the U. S. Natural Rubber Research Station on October 23, 1950. Dr. Le Bras has long been associated with research on physical testing, oxygen absorption, aging, and related topics pertaining to natural rubber. These subjects were discussed with him. He was shown our oxygen absorption apparatus which is similar to that used by other workers. The problem of supporting a crude guayule rubber sample in this apparatus, to prevent its deformation during the conduct of an aging test, was one that had not been solved at the time. Dr. Le Bras offered suggestions for overcoming this difficulty.

The selection and use of antioxidants were discussed, with particular reference to the protection of natural rubber. The protection of vulcanized rubber, where antioxidants are mostly used, is not the same as with crude rubber. It is known, for example, that some substances which act as antioxidants for vulcanized rubber actually accelerate oxidation of crude rubber. Oxygen absorption on vulcanized Hevea rubber was stated by Dr. Le Bras as not being necessarily correlated with quality deterioration on aging.

Dr. Le Bras was informed of the fact that guayule rubber appears to develop higher heat build-up than Hevea rubber, in the hope of learning his opinion as to the possible cause of this defect. He believed it was tied up with molecular weight relationships, but no definite answer was known. He suggested that we operate our compounding rolls at a higher than normal temperature in order to partially off-set the rapid breakdown on the mill during compounding. Guayule rubber breaks down so rapidly on milling that dispersion and incorporation of compounding ingredients may not be sufficiently thorough before breakdown goes too far. Higher mill temperatures increase plasticity without so much breakdown.

Analytical methods for the determination of rubber hydrocarbon and metals were also discussed. Dr. Le Bras showed great interest in the improvement we had made along these lines.

It was stated by Dr. Le Bras that rubber production in Indo-China was less than half of the potential (40 to 45 thousand tons out of a possible of about 100 thousand) because of Communistic influences. Endeavors of the French to improve uniformity of plantation rubber through grading according to physical properties were described.

7. Other

Dr. Norberto Reichart, Director General of Agriculture, Buenos Aires, Argentina, visited the U. S. Natural Rubber Research Station on January 24, 1948 for the purpose of discussing guayule rubber production and to obtain some general information concerning the program of work from both BAIC and BPIS&AE. The various laboratories, pilot plant, and field plantings were shown to Dr. Reichart. Information was obtained from Dr. Reichart that about 600 to 800 acres (irrigated) were then planted to guayule in Argentina. However, no work seemed to be in progress on rubber extraction, but some experiments were devoted to cultivation of guayule.

Miss Madan L. Devan, Soil Technologist, Department of Agriculture, India, visited on February 24, 1948, to obtain general information, primarily from BPIS&AE.

Mr. L. Vaitzman, Head of the Section of Industrial Plants, Ministry of Agriculture, Tel-Aviv, Israel; and Mr. I. Gutstein, Research Assistant, Division of Agronomy and Plant Breeding, Hebrew University, College of Agriculture, Rehovot, Israel, visited Salinas on May 22, 1950. These men were making a 10-month tour of the United States in the interests of agriculture in Israel. Although they were primarily interested in the cultural and breeding work on guayule under investigation by BPIS&AE, interest was also expressed in guayule extraction and processing procedures.

Mr. J. C. Mathison, rubber planter from Johore, Malaya, visited the Station in company with Mr. Warren Lockwood, Director, Natural Rubber Bureau, Washington, D. C., on April 1, 1951, to observe guayule culture and processing operations. The Natural Rubber Bureau is sponsored by the British Rubber Development Board, and its function is to promote the use of natural rubber in the United States. Mr. Mathison, in addition to being a rubber plantation owner in Malaya, is also a member of the legislative council and a board member of the Rubber Research Institute at Kuala Lumpur.

Miss F. A. M. Hoffmann of the Instituto de Pesquisas Tecnologicas, Sao Paulo, Brazil, included the Salinas Laboratory on October 22, 1951, in her tour of various laboratories in the United States in search of new methods and equipment for application in Brazilian technology.

Mr. Rees Davies, Agricultural Attache, South African Embassy, Washington, D. C., visited the Station on November 6, 1951. It was learned that a number of experimental plots of guayule were being grown in South Africa with a view to exploring the potential possibilities of producing this source of rubber in the event normal supplies of rubber were cut off. Mr. Davies indicated that he was primarily interested in cultural and genetic developments, but was pleased to learn of the extraction work in progress and of the advances made with respect to rubber quality improvement.

Inquiries were received from a number of foreign countries, or organizations representing foreign interests, to obtain information on the culture and processing of guayule, and to receive reprints of publications. Those inquiries pertaining to requests for seed or the culture of guayule were, of course, handled by BPIS&AE.

The American Economic Committee for Palestine, Inc., New York City, for example, requested general information on guayule in January 1948. It was stated that Palestine had in mind the cultivation of guayule in the Negev or the southern desert area of this country.

Other countries not already mentioned elsewhere in this report from which correspondence was received included Egypt, Germany, Norway, Switzerland, and Portugal.

C. Industrial Testing and Evaluation of Deresinated Guayule Rubber

1. Preparation and Distribution of Sample Lots

The enlistment of industrial cooperation in guayule rubber quality evaluation was considered to provide the most important means of supplementing the work at Salinas, and of assessing the progress that had been made in quality improvement through the processing of freshly harvested shrub in combination with deresination of the crude rubber, incorporation of antioxidants and other innovations.

Various sample lots of deresinated guayule rubber, varying in quantity from 5 to 2500 pounds and totaling nearly 9000 pounds, were prepared from time to time for distribution as requested by different cooperating industrial organizations. The cooperating members (listed in Table 5) include the major rubber manufacturers, as well as smaller companies, and comprise an excellent representation of the entire American rubber industry.

The composition of the different lots of rubber, together with an indication of the purpose of each test, are also shown in Table 5. Typical results of physical tests on deresinated guayule rubber as carried out at Salinas are shown in Table 6. Shrub used for extraction of all the rubber samples was of Variety 593.

2. Laboratory and Related Tests

Reports of test results and related information received from the cooperating industries are summarized under the cooperating organization headings as follows:

a. Accurate Products Company, Pacific Beach Station, San Diego, Calif.

This company is a small manufacturer of molded rubber goods such as gaskets, hot water bottles, etc., who became interested in the use of guayule for manufacture of these products. A sample bale of deresinated rubber was forwarded on request. Although no written report of tests was received, Mr. J. G. Wilson, President of the Company, stated verbally that he was highly

Table 5. Distribution of Sample Lots of Deresinated Guayule Rubber for Industrial Testing and Evaluation

Date	Cooperating Industry	Amount	Shrub Age	Shrub Field	Resin	Alcohol-Benzene Insolubles	Rubber hydrocarbon	Added Antioxidant	Mooney ML 212° F.	Deresination Method	Purpose of Test
		Pounds	Years		Percent	Percent	Percent	Percent			
12/21/50	Armstrong Rubber Co.	10	7	Spence	1.45	6.42	92.13	0.5 PBNA	102	Worm	Gen'l lab. evaluation
6/5/51	Accurate Products Co., Inc.	45	9	Guidotti	1.30	3.73	93.7	1.25 "	89	"	" " "
4/17/51	Armstrong Rubber Co.	25	9	Guidotti	2.43	4.82	92.05	0.70 "	91	"	" " "
7/23/51	" " "	1300	7	Spence	1.30-2.39	3.30-4.55	--	0.25-1.38 "	94-97	"	Mfg. truck tires
8/28/52	" " "	1500	8	Spence	1.73-2.36	4.38-5.61	--	0.40-0.67 ARW	92-99	"	" " "
4/6/51	Army Chemical Center	5	9	Guidotti	1.83	5.0	92.2	1.0 PBNA	88	"	Gas mask face blanks
12/8/52	Carlisle Tire & Rubber Co.	25	8	Spence	2.0	4.8	92.7	0.5 ARW	97	"	Pre-test f/airplane tubes
8/29/50	Firestone Tire & Rubber Co.	2	-	--	2.75	5.5	90.75	1.0 ARW	97	Shrub	Gen'l lab. evaluation
8/8/50	" " " "	5	8	Guidotti	2.0	5.3	91.5	1.0 PBNA	98	Worm	" " "
8/8/50	" " " "	100	8	Guidotti	2.74	5.71	89.1	1.0 PBNA	98	Shrub	" " "
11/30/50	" " " "	1 gal	(latex) Total solids 51.6 g./100 ml.; ethanol solubles 4.2 g./100 ml.							one	and tire tread road test Electron microscope exam., foam rubber preparation
3/20/51	" " " "	10	9	Guidotti	2.19	5.60	91.8	0.41 PBNA	91	Worm	Gen'l lab. evaluation
4/17/51	" " " "	25	9	Guidotti	1.91	4.60	92.75	0.75 PBNA	91	"	Pre-test to tire mfg.
10/29/52	" " " "	25	8	Spence	2.36	5.58	91.7	0.32 ARW	96	"	Pre-test f/airplane tires
4/26/51	" " " "	1300	9	Spence	1.7-2.3	4.2 - 5.2	--	0.6-1.0 PBNA	90-92.5	"	Mfg. truck tires
10/28/52	General Tire & Rubber Co.	25	8	Spence	2.08	5.92	91.7	0.28 ARW	99	"	Gen'l lab. evaluation
3/20/51	B. F. Goodrich Co.	10	9	Guidotti	2.19	5.60	91.8	0.41 PBNA	91	"	" " "
10/28/52	" " " "	25	8	Spence	1.74	5.70	92.0	0.56 ARW	97	"	" " "
6/16/50	Goodyear Tire & Rubber Co.	6						1.0 PBNA	95	Shrub	Molecular wt. studies &
"	" " " "	Miscellaneous molecular weight fractions									dynamic properties
3/20/51	" " " "	10	9	Guidotti	2.19	5.60	91.8	0.41 PBNA	91	Worm	Dynamic properties
4/17/51	" " " "	25	9	Guidotti	2.43	4.82	92.05	0.70 PBNA	91	"	Pre-test to tire mfg.
6/5/51	" " " "	1300	9	Guidotti	1.25-2.50	2.50-4.50	--	0.6-1.3 PBNA	90-95.5	"	Pass. car tire mfg.
10/29/52	" " " "	25	8	Spence	1.98	5.14	92.5	0.38 ARW	99	"	Pre-test f/airplane tires
8/5/52	General Tire & Rubber Co.	5	8	Spence	2.3	5.0	92.0	0.7 ARW	94	"	Gen'l lab. evaluation
10/28/52	" " " "	25	8	Spence	2.08	5.92	91.7	0.28 ARW	99	"	" " "
7/27/51	Hewitt-Robins, Inc.	10	7	Spence	1.78	3.65	93.7	0.81 PBNA	93	"	" " "

(continued)

Table 5 (continued) Distribution of Sample Lots of Deresinated Guayule Rubber for Industrial Testing and Evaluation

Date	Cooperating Industry	Amount	Shrub Age	Shrub Field	Resin	Alcohol-Benzene Insolubles	Rubber hydrocarbon	Added Antioxidant	Mooney ML 212° F.	Deresination method	Purpose of test
		Pounds	Years		Percent	Percent	Percent	Percent			
3/20/51	Johnson & Johnson	5	9	Guidotti	2.19	5.60	91.8	0.41 PBNA	91	Worm	Lab. test f/adhesives
11/13/50	Mellon Inst. of Indus. Res.	5			1.5	5.1	91.0	1.0 PBNA	93	"	Fundamental properties
7/23/52	Nat'l Bur. of Standards	60	8	Spence	2.0	6.0	91.5	0.5 ARW	93	"	Vulcan. characteristics
4/19/49	" " " "	6	4-5	Spence	Misc. samples extracted from different plant fractions						Low temp. "
8/15/50	W. J. Voit Rubber Corp.	5	8	Guidotti	2.0			1.0 PBNA	93.5	Shrub	Gen'l lab. evaluation
9/20/50	" " "	5	8	Guidotti	0.85	5.95	92.7	0.9 Ionol	102	Worm	" " "
9/20/50	" " "	5	8	Guidotti	20.7	6.39	72.6	0.9 Ionol	55	None	" " "
12/21/50	Precision Rub. Prod. Corp.	5	8	Guidotti	1.49	5.21	93.3	0.5 PBNA	103	Worm	Test for use in O-rings
12/21/50	" " " "	5	8	Guidotti	26.48	4.89	68.6	1.5 PBNA	36.5	None	" " " " "
10/29/52	F. G. Schenuit Rubber Co.	50	8	Spence	1.7- 1.8	5.1 -5.5	92.0	0.5-0.6 ARW	95-97.5	Worm	Pre-test f/airplane tires
2/20/53	" " "	2500	8	Spence	1.7- 2.5	4.4 -5.8	--	0.3-0.7 ARW	93-100.5	"	Airplane tire mfg.
8/5/52	Mohawk Rubber Co.	5	8	Spence	2.3	5.0	92.0	0.7 ARW	94	"	Gen'l lab. evaluation
8/5/52	Seiberling Latex Prod. Co.	5	8	Spence	2.3	5.0	92.0	0.7 ARW	94	"	" " "
8/5/52	New York Rubber Corp	5	8	Spence	2.3	5.0	92.0	0.7 ARW	94	"	" " "
8/5/52	Raybestos-Manhattan, Inc.	5	8	Spence	3.2	4.0	92.3	0.5 ARW	91.5	"	" " "
8/5/52	Hood Rubber Co.	5	8	Spence	3.2	4.0	92.3	0.5 ARW	91.5	"	" " "
8/5/52	The Okonite Co.	5	8	Spence	2.3	5.0	92.0	0.7 ARW	94	"	" " "
4/17/51	Gov't Lab., Univ. of Akron	25	9	Guidotti	1.91	4.6	92.7	0.76 PBNA	91	"	" " "
4/19/49	" " " " "	60	4-5	Spence	Misc. samples extracted from different plant fractions						Low temp. characteristics
7/23/52	" " " " "	50	9	Guidotti	2.0	6.0	91.5	0.5 ARW	93	"	Gen'l lab. evaluation
11/15/51	Sun Rubber Co.	20	9	Guidotti	1.9	3.2	93.9	1.0 PBNA	95	"	" " "
11/7/51	Surety Rubber Co.	50	9	Guidotti	1.25	3.5	94.5	0.75 PBNA	96	"	Test f/elect. gloves
9/10/52	" " "	50	8	Spence	2.38	5.22	91.83	0.57 ARW	94	"	" " "
9/26/52	U. S. Rubber Co.	20	8	Spence	2.0	5.0	92.5	0.5 ARW	100	"	Pre-test f/airplane tires
7/12/51	" " " "	25	7	Spence	2.06	3.8	93.3	0.87 PBNA	94	"	Gen'l lab. evaluation
10/29/52	" " " "	25	8	Spence	1.86	5.47	92.1	0.53 ARW	99	"	Pre-test f/airplane tires
	U. S. Naval Rubber Lab.	60	Miscellaneous samples for low temperature testing								
11/21/52	" " " " "	50	8	Spence	2.06	5.47	91.9	0.81 ARW	97.5	"	Gen'l lab. evaluation
4/19/49	World Bestos Corp.	30		Spence	Misc. samples extracted from different plant fractions						Test f/brake lining

PBNA = Phenyl-beta-naphtnylamine

ARW = Di-beta-naphthyl-para-phenylene-diamine

ial Testing and Evaluation

Added ntioxidant	Mooney ML 212° F.	Deresin-ation method	Purpose of Test
Percent			
0.41 PBNA	91	Worm	Lab. test f/adhesives
1.0 PBNA	93	"	Fundamental properties
0.5 ARW	93	"	Vulcan. characteristics
ifferent plant fractions			Low temp. "
1.0 PBNA	93.5	Shrub	Gen'l lab. evaluation
0.9 Ionol	102	Worm	" " "
0.9 Ionol	55	None	" " "
0.5 PBNA	103	Worm	Test for use in O-rings
1.5 PBNA	36.5	None	" " " " "
5-0.6 ARW	95-97.5	Worm	Pre-test f/airplane tires
3-0.7 ARW	93-100.5	"	Airplane tire mfg.
0.7 ARW	94	"	Gen'l lab. evaluation
0.7 ARW	94	"	" " "
0.7 ARW	94	"	" " "
0.5 ARW	91.5	"	" " "
0.5 ARW	91.5	"	" " "
0.7 ARW	94	"	" " "
0.76 PBNA	91	"	" " "
ifferent plant fractions			Low temp. characteristics
0.5 ARW	93	"	Gen'l lab. evaluation
1.0 PBNA	95	"	" " "
0.75 PBNA	96	"	Test f/elect. gloves
0.57 ARW	94	"	" " "
0.5 ARW	100	"	Pre-test f/airplane tires
0.87 PBNA	94	"	Gen'l lab. evaluation
0.53 ARW	99	"	Pre-test f/airplane tires
sting			
0.81 ARW	97.5	"	Gen'l lab. evaluation
fferent plant fractions			Test f/brake lining

nine

Table 6. Typical Physical Test Results of Deresinated Guayule Rubber in Gum Formulas

(BAIC, Natural Rubber Extraction and Processing Investigations)

Minutes cured at 275° F.	STRESS @ 500% Elong.	STRESS @ 600% Elong.	Tensile Strength
	p.s.i.	p.s.i.	p.s.i.
	Formula A 1/		
30	280	480	2320
40	420	780	2930
60	520	1000	3420
80	570	1040	3245
	Formula B 1/		
25	340	610	2770
30	470	940	3150
40	640	1270	3720
60	670	1440	3450
80	730	1510	3410

1/ Compounding recipes:

	Formula A	Formula B
Rubber	100	100
Stearic acid	6.0	4.0
Zinc oxide	4.0	4.0
Sulphur	3.5	1.5
Benzothiazyl disulfide	1.0	1.0
Methyl thiuram disulfide	---	0.15

impressed with the possibilities of such rubber. He became so enthusiastic, in fact, that the company established a planting of guayule with the intent of producing a quantity of rubber as an independent source of supply for their own factory use.

b. Armstrong Rubber Company, West Haven, Connecticut. Preliminary tests on a 10-pound sample of worm deresinated rubber indicated slower curing and generally lower physical properties as compared with Hevea. However, in compounding, the regular ACS #1 and ACS #2 formulas were used and guayule was merely substituted for Hevea in these formulas - apparently without attempt to make any specific adaptations for guayule. Thus, it seems likely that insufficient acceleration was used in the case of guayule and the latter, therefore, suffered in the comparison of tensile values and other properties. With regard to cut flex and aged modulus, aged tensile and aged cut flex, the guayule was shown to be either better or as good as Hevea in a carcass stock formulation. Guayule was inferior to Hevea in heat rise (heat build-up) as measured on the Goodrich flexometer. It was concluded that the guayule rubber would be suitable for use in tire carcasses.

This Company subsequently participated in Government Tire Test Project "CV", in which deresinated guayule rubber was compared with Hevea rubber with respect to performance and serviceability when used in the fabrication of heavy-duty truck tires. A more detailed discussion of these tire tests will be found later under a separate heading.

c. Army Chemical Center, Maryland, Chemical and Radiological Laboratories, Chemical Corps. This organization was engaged in research designed to replace or drastically reduce the Hevea rubber content of gas mask face blanks. Most of their attention was centered around the possible use of butyl and GR-S or other synthetics. A 5-pound sample of deresinated guayule rubber was submitted at their request for evaluation. However, since they stated that practical consideration could be given only to polymers in the light of their availability in the foreseeable future, it is doubtful that the guayule rubber was given any serious attention. No report was received.

d. Firestone Tire & Rubber Company, Akron, Ohio. A number of samples of deresinated guayule rubber were submitted at various times, as indicated in Table 5. A sample of latex was also included. This was used for electron microscope observation, and also for preparation of foam rubber. A report of the results obtained on the latex is given under "Latex Investigations".

A comparison was made between shrub deresinated and worm deresinated guayule rubber. Physical tests were made on four standard test formulas: (1) ACS formula; (2) ACS #1-A containing higher stearic acid; (3) tire body stock accelerated with MBT (mercapto-benzo-thiazol) accelerators; and (4) tire tread stock accelerated with MBT accelerators. Both normal and aged tests were made. The following conclusions were reported by the Company:

1. The modulus and tensile strength for both the worm and shrub deresinated guayule rubbers were lower than for the #1XRSS (No. 1 Ribbed Smoked Sheet), a premium grade

of Hevea rubber used for comparison.) The worm deresinated sample had the lowest physical properties.

2. Properties of both samples of guayule were enhanced by the additional stearic acid in ACS #1-A compounding formula to a much greater degree than the #1XRSS, as evidenced by the increased modulus and tensile figures. This was to be expected, as the deresination would remove any organic acids present in the guayule which might normally activate the accelerator.

3. When tested in the tire body stock containing the self-activating MBT accelerator, both the worm and shrub deresinated samples responded in a normal manner and showed a substantial increase in physical properties.

4. Only the shrub deresinated guayule was compared with #1XRSS in the tire tread stock. The guayule was somewhat inferior in respect to tensile strength but was practically equal in modulus. The flexometer evaluation showed that the guayule tread is much less efficient than the #1XRSS tread and would produce a tire with a hotter running temperature.

5. The artificial aging tests indicated that both samples of guayule held up equally as well as the #1XRSS in the ACS, ACS #1-A and tire body stock, while the shrub deresinated guayule appeared to be slightly inferior to the #1XRSS in the tire tread stock.

6. Summarizing these conclusions, it is apparent that the shrub deresinated guayule is superior to the worm deresinated guayule, but is not equal to standard smoked sheets.

Despite the poorer showing of the worm deresinated sample, there seemed to be no reason for its inferiority except as caused through degradation in the newly developed resin extraction procedures. Further experiments on worm deresination have indicated that a rubber with Mooney and tensile values equivalent to those of shrub deresinated rubber may be obtained. Accordingly, a second sample (5 pounds) of worm deresinated rubber was submitted for test. Physical properties of this lot was compared with those of a 100-pound lot of shrub deresinated rubber and with those of Liberian Pale Crepe. Modulus and tensile strength values were slightly higher for the worm deresinated rubber; both shrub and worm deresinated rubbers were somewhat inferior to the Hevea rubber. Results of the tests with the tire body stocks are shown in Table 7.

Table 7. Comparison of Worm Deresinated and Shrub Deresinated Guayule Rubbers with Hevea No. 1 Ribbed Smoked Sheet in Tire Body Stocks (as reported by the Firestone Tire & Rubber Co.)

Cured @ 260° F.	30 Min. Cure		60 Min. Cure		90 Min. Cure	
	Mod. @ 600 % Elong.	Tensile	Mod. @ 600 % Elong.	Tensile	Mod. @ 600 % Elong.	Tensile
	p.s.i.	p.s.i.	p.s.i.	p.s.i.	p.s.i.	p.s.i.
Normal Tests						
Worm deresinated guayule	1900	2525	2700	3625	2700	3650
Shrub deresinated guayule	2275	3375	2625	3825	2650	3725
Hevea #1RSS	2675	4275	3275	4475	3350	4175
Aged 7 days @ 158° F.						
Worm deresinated guayule	2775	3975	3375	3875	3700	3700
Shrub deresinated guayule	3700	4075	3800	4200	3650	3725
Hevea #1RSS	3825	4475	4175	4175	--	3825

The 100-pound lot of shrub deresinated rubber was used for the fabrication of treads on two experimental passenger car tires. Hevea rubber comprised half the tread and guayule the other half of each tire. Road tests were made by the Government Fleet and wear was checked at 12,305 miles. It was reported that the guayule rated 82% of the Hevea rubber for wear, and that there was no difference in cut growth and tread cracking. Performance was satisfactory for the total mileage run of 14,494 miles. This was regarded as a fairly good showing and that the guayule was comparable in tread wear to the regular GR-S used during World War II.

On the basis of the evident comparable quality of worm deresinated and shrub deresinated, a decision was made to provide sufficient worm deresinated rubber for heavy-duty truck tire tests. It would not have been possible to produce such quantities of shrub deresinated rubber with the available equipment, and the early demonstration of high quality of worm deresinated rubber enabled the truck tire testing program to proceed without delay. A 1300-pound lot of worm deresinated rubber was provided the Company in April 1951. A report of truck tire tests is given elsewhere.

e. General Tire & Rubber Company, Akron, Ohio. A 25-pound sample of worm deresinated guayule rubber was provided this Company in October 1952. This was tested in a typical natural rubber carcass compounding recipe by a direct substitution of the smoked sheet rubber (No. 3 Ribbed Smoked Sheet) normally used. In one case, stearic acid was increased in the formula to compensate for the fatty acid deficiency in the deresinated guayule. Results of physical tests were summarized as follows:

1. Deresinated guayule has the same cure rate as #3RSS in a carcass recipe.

2. The guayule has approximately 250 pounds per square inch lower maximum tensile strength than #3RSS in carcass stock.

3. The guayule carcass stock has higher tear resistance than the #3RSS carcass stock.

4. The guayule carcass stock has better aging properties depicted by higher retained tensiles after oven aging.

5. Increasing stearic acid in the guayule stock to 6.0 parts has no beneficial effect.

6. The guayule had a Mooney viscosity similar to that of the #3RSS.

The conclusion was drawn that "the deresinated guayule is a high grade form of rubber hydrocarbon, suitable for carcass stocks".

f. B. F. Goodrich Company Research Center, Brecksville, Ohio. A 10-pound sample of deresinated guayule rubber was tested for comparison of physical properties with those of a typical grade of natural rubber, in this case a technically classified Hevea designated as "Yellow X", according to the French system of classification. It can be considered as being equivalent to No. 1 Smoked Sheet in this study. Both gum and carbon black compounding formulas were used.

When compound recipe adjustments were made to compensate for the absence of fatty acids in the guayule, vulcanizates of excellent quality were obtained having stress-strain properties nearly equal to that of the controls. The guayule stocks were somewhat inferior with respect to hysteresis and the carbon black guayule stock was somewhat poorer in resistance to flex cracking than the control. Stocks of both rubbers behaved similarly on aging, except that the modulus of the guayule gum stock remained nearly constant whereas that of the control increased.

The rate of breakdown of the crude guayule rubber on mastication at 150° C. was appreciably greater than that of the Hevea rubber.

In another investigation, a lot of deresinated guayule was supplied to the B. F. Goodrich Company for preliminary testing in airplane tire coat stock and tread stock. The conclusion reported was that "generally speaking, the deresinated guayule supplied was found to be nearly equivalent to Hevea #2RSS (Ribbed Smoked Sheet)".

g. Goodyear Tire & Rubber Company, Akron, Ohio. Molecular weight comparisons of deresinated guayule rubber were made with pale crepe, smoked sheet Hevea rubbers, and GR-S. Calculations of molecular weight were made from intrinsic viscosity measurements of benzene solutions. The results are reported in Table 8.

Table 8. Molecular Weight of Deresinated Guayule Rubber as Compared with Hevea and GR-S (Goodyear Tire & Rubber Company)

Sample	Intrinsic Viscosity		Calculated Molecular Weight 1/	
	4-pass milling	10-pass milling	4-pass milling	10-pass milling
Guayule	3.12 2/	2.01	491,000	254,000
Smoked sheet	3.04 2/	2.64	472,000	382,000
Pale crepe	3.62	2.35	614,000	321,000
GR-S	(1.8-2.0)		(215,000 to 252,000)	

1/ From the Scott-Magat relations for Hevea: Log M = 4.95 + 1.5 log (n) in which M = number average molecular weight and (n) = intrinsic viscosity.
2/ Some gel still present after four passes.

These results show that guayule has a molecular weight of the same order of magnitude as Hevea. The 10-pass milling result indicates that the guayule may undergo a faster rate of breakdown than pale crepe or smoked sheet.

Dynamic tests were also made on vulcanized test pieces using compression vibrations; 60 cycles per second. The dynamic stiffness of the guayule compound was practically identical to that of the Hevea compound, but the internal friction of the guayule was considerably greater so that the resilience was lower - causing greater heat generation. In gum stocks, the resilience for Hevea and guayule were 58 and 47.5 percent, respectively. For tread stocks, the corresponding figures were 33.2 and 26.8 percent. Efforts were then made to measure the dynamic properties of raw guayule in special equipment devised at Goodyear. To improve adhesion of the specimen used in the tests, guayule was masticated. This gave poor dynamic values. The resilience was reported as only 22 percent. This may have been due to excessive breakdown on mastication. Infrared examination of the masticated raw guayule showed pronounced evidence of oxidation, the OH and CO bonds being quite prominent. Direct analysis for oxygen gave an average value of 4.6 percent. This is surprising in view of the fact that it is known that the absorption of as much as 1% oxygen will cause crude rubber to become practically fluid and thus completely degraded.

It was also thought that heat build-up in guayule might be caused by its particular molecular weight distribution. In order to obtain further information on this point, several molecular weight fractions of the rubber were prepared by fractional precipitation with acetone from benzene solution including (1) a high molecular weight fraction; (2) a low molecular weight fraction; (3) an unfractionated undissolved control; and (4) an unfractionated, dissolved, and precipitated control. These samples were tested without

mastication to determine the dynamic shear modulus, the internal friction, and the resilience. Results are shown in Table 9.

Table 9. Dynamic Properties of Raw Guayule and Hevea Rubbers (Goodyear Tire & Rubber Company)

Materials	Dynamic Shear Modulus	Internal Friction	Resilience
	Kilograms/cm^2	Kilopoises	Percent
Raw guayule rubber			
High molecular weight fraction	4.46	.534	74.8
Low molecular weight fraction	3.40	.715	60.2
Dissolved, unfractionated	4.51	.642	70.8
Undissolved, unfractionated	4.24	.628	69.9
Hevea smoked sheet	4.30	.740	65.9

These data show that guayule has dynamic properties similar to those of the Hevea sample, with the high molecular weight fraction being superior to the low molecular weight fraction. Subsequently, these fractions and controls were compounded in tread stocks and dynamic properties were determined on the vulcanizates. The results are shown in Table 10.

Table 10. Dynamic Properties of Tread Stocks of Guayule and Hevea Rubbers (Goodyear Tire & Rubber Company)

Materials	Dynamic Compression Modulus	Internal Friction	Resilience
	Kilograms/cm^2	Kilopoises	Percent
Guayule rubber			
Low molecular weight fraction	107.4	56.8	27.8
High molecular weight fraction	127.3	67.7	27.6
Undissolved, unfractionated	137.0	69.2	31.0
Dissolved, unfractionated	105.8	52.2	30.3
Earlier tests			
Hevea	127	55.8	33.2
Guayule	127	66.2	26.8

As in the case of the raw rubbers shown in the preceding table, the vulcanized stocks of guayule compared much more favorably with Hevea than in the earlier tests.

A 25-pound sample of deresinated rubber was submitted to Goodyear for the conduct of tests preliminary to experimental manufacture of passenger car tires. In these tests a carcass stock formula was used. Hevea/GR-S mixtures and Guayule/GR-S mixtures were used as well as a Hevea control. Ultimate tensile values for the guayule were over 4000 p.s.i., which appeared to be the highest reported by any of the industrial cooperators, and were essentially equivalent to corresponding values for Hevea. The guayule was superior in the cold rebound test but inferior in the hot rebound test. In the Goodrich flexometer test guayule was indicated to be inferior to Hevea with respect to heat rise. The 50-50 mixture of guayule and GR-S, however, had no higher heat rise than the 50-50 mixture of Hevea and GR-S. The significance of the flexometer tests in this case is uncertain. It was thought that the extent of mastication during compounding affected the heat build-up as suggested from the results of previous work. However, information obtained later on this point indicated that the Hevea and the guayule received the same (minimum) mastication. Guayule was shown to hold up as well as Hevea in an aging test.

h. Government Laboratories, University of Akron, Akron, Ohio. A group of guayule rubber samples was submitted to the Government Laboratories for the investigation of low temperature properties, following a suggestion by Mr. John Caswell that guayule, by virtue of its lower molecular weight, might be better suited than Hevea rubber for service under low temperature conditions such as exist in the Arctic. The results of this study are reported under a special heading.

Further evaluation of deresinated guayule was made in comparison with Hevea rubber. Both materials were compounded according to gum, tread, and carcass type recipes. Certain synthetic polymers were also included for test in the black stocks.

In the gum vulcanizates, it was reported that the quality of guayule approached closer to Hevea than in either of the other two types of stock. Less than 10 percent difference existed in either their maximum or average tensile strength values; and no significant advantage is shown for Hevea in either hysterisis or cut-growth properties. Rebound data favored Hevea compounds at room temperature, but almost identical rebounds were obtained at 212° F. The low temperature flexing characteristics of the two compounds were similar.

In the tread type recipe, the guayule compound extruded better than did the smoked sheet. This is an important advantage in processibility from the standpoint of the rubber manufacturer. The tensile strength of the guayule in the tread stock averaged 92 percent as high as those for Hevea. Cut growth resistance values were equivalent. Rebound values were highest for the Hevea. Low temperature flexibility tests indicated slight superiority for the Hevea only during the initial stages of stiffening. Abrasion resistance of the two rubbers was equivalent although much inferior to that of cold GR-S.

In the carcass compounds, the Hevea vulcanizates yielded outstanding values for stress-strain, hysteresis, and resilience. Cut growth resistance and percentage retention of room temperature tensile strength at 212° F. were equal for the Hevea and guayule compounds.

It should be pointed out, however, that the comparisons between guayule and Hevea in this study are not based upon an exhaustive compounding investigation. Only one formula each for the gum, tread, and carcass stock was used and the only apparent difference in the recipe used for guayule, as compared with that used for Hevea, was in the amount of stearic acid. This can hardly be expected to bring out the best properties for guayule rubber under all conditions, although an attempt was made to provide data for comparable states of cure. In later work, the Government Laboratories reported that slight changes in the guayule recipe produced comparatively large changes in physical properties.

i. Hermann Weber & Company, Inc., New York, N. Y. This company operates a large plant for the deresination of Balata, Gutta Percha and kindred gums. Because of their experience in this field, they became interested in the deresination of guayule rubber and expressed a wish to cooperate on this problem.

A fresh lot (approximately 15 pounds, dry basis) of resinous rubber worms, submerged in water, was shipped to New York for trial of the Hermann Weber & Co. process. A letter of information accompanied the shipment which pointed out that the worms must not be allowed to dry before deresination in order to avoid degradation and difficulty of solvent extraction.

No detailed information was received concerning the process of deresination that was used. The following is quoted from a letter of September 18, 1951 from Mr. C. E. Wegmann addressed to Mr. C. F. Speh, Assistant Chief, AIC:

> "Using cold acetone, we made four extractions of twelve hours each, after which the rubber was allowed to dry and all traces of the acetone removed. This rubber was milled up and 1% of AgeRite (antioxidant) included. This was the last sample submitted and of this quantity we still have on hand a balance of seven pounds."

The first sample of deresinated rubber that was received from Hermann Weber & Co. appeared to be badly degraded. Our analysis gave the following figures:

Ethanol solubles (resins)	2.35%
Ethanol and benzene insolubles	5.77%
Rubber hydrocarbon (direct determination)	85.57%

The low content of resin indicates that a reasonably satisfactory deresination was accomplished, although our value may be somewhat inaccurate due to difficulties in preparing and handling the sticky sample. The rubber hydrocarbon content is considered low since we usually expect around 92 percent in samples with a comparable content of resins and insolubles. Evidently the low rubber hydrocarbon content (as determined by the bromination method) is due to the degraded condition of the rubber, i.e., partial oxidation that resulted in a low bromination value. It is obvious that some means of pro-

tecting the material would have to be found before the product could be considered acceptable.

The second sample of deresinated rubber, which is referred to in the above quotation, was much better in appearance than the first one and did not exhibit the extreme stickiness of the latter. However, the material was much softer than our product as shown by the very low Mooney viscosity value of 28. Our deresinated rubber usually has a Mooney value of 90 or above. This softness is probably due to degradation at some point in the process. The completeness of deresination was not as good as in the case of the first sample but might still be considered fair. Our analyses follow:

Ethanol solubles (resin)	4.01%
Ethanol and benzene insolubles	5.16%
Rubber hydrocarbon (direct determination)	90.45%
Mooney viscosity (ML 212°F. at 4 min.)	28

j. Hewitt-Robins Inc., Hewitt Rubber Division, Buffalo, N.Y. A 10-pound sample of deresinated guayule rubber was tested by this company with a view to determining its suitability for use as a natural rubber in top quality conveyor belt cover compounds. Such a stock is very similar to a natural rubber tire tread stock, and is comparable in resistance to abrasion, tensile properties, elongation, etc. It contains 40 parts of carbon black. A gum recipe was also used in compounding for comparison with Hevea rubber control. The grade of Hevea rubber used was No. 2 Ribbed Smoked Sheet.

It was concluded that the guayule rubber appeared to be very similar to the Hevea control in all of its properties, when the cure rates of the materials and variations in physical properties of Hevea from shipment to shipment are given consideration.

The guayule had a slightly slower curing speed than the Hevea under similar conditions. It was remarked that "The sample submitted represents the best quality of deresinated guayule which has come to my attention during the 35 years in which the writer has been associated with the rubber manufacturing industry".

k. Johnson & Johnson, New Brunswick, New Jersey. A 5-pound sample was sent to this company in response to their request due to their interest in deresinated guayule for comparison with Hevea rubber in the production of surgical adhesive tapes. Their report of January 30, 1952 stated that while the deresinated guayule was substantially better than the resin-containing guayule which they had previously had experience with, it still did not compare favorably with Hevea rubber. No further information was reported.

l. Mellon Institute of Industrial Research, Pittsburgh, Pa. A research unit of this organization, sponsored by the Office of Rubber Reserve, became interested in guayule rubber in connection with the conduct of fundamental studies on the relationships between the molecular structure and physical properties of synthetic rubbers.

A sample of deresinated guayule rubber was furnished for comparison with other rubbers. Unfortunately, very little work was actually performed.

However, the infrared spectrum was reported to be identical with that of Hevea. This is a confirmation of previous findings with guayule rubber.

m. National Bureau of Standards, Washington, D. C. Various cooperative tests were made by the National Bureau of Standards. One of the first problems to be investigated was the incorporation of GR-S with guayule.

GR-S is inferior with respect to the highly desirable property of tackiness in relation to proper adhesion of rubber to fabrics such as in the manufacture of footwear, belting, and tire sidewalls. Guayule rubber, on the other hand, is comparatively quite tacky and it was thought possible to improve the tack and possibly other properties of GR-S by the incorporation of a certain amount of guayule rubber.

GR-S and guayule latices were used in this investigation. A progress report indicated that it was first necessary to study coagulating characteristics of these latices and of their mixtures. Zinc acetate was found to serve as a good coagulant without having degrading effects. The addition of protective colloids, such as sodium alginate, to the latices before addition of the coagulant produced a coagulum with a crumb structure which favored more rapid washing and drying.

An instrument designed to measure tackiness was constructed, but it was found necessary to devote considerable time to standardization of procedure in order to obtain reproducibility of measurement. No definite conclusions were reached before the work was curtailed.

Some cooperative work was done on the analyses of guayule rubber samples for content of trace metals in order to evaluate the suitability of existing analytical methods. The results indicated good agreement by the method in use at Salinas; and that the procedure of ashing samples in the furnace does not result in loss of metals.

A sample of deresinated guayule rubber was submitted for trial in work on the impregnation of sole leather for shoes to improve wear and moisture resistance. In these studies, solutions of various rubbers were used to impregnate the leather. It was concluded from preliminary trials with guayule that this product would probably not serve any better than Hevea rubber. However, since the rubbers must be broken down catalytically to a point where concentrated benzene solutions of low viscosity can be made, it is possible that the guayule might offer an advantage with respect to rate of breakdown. In rubber-impregnated leathers, water absorption is about one-half of that of untreated leathers - and wear is increased 75 to 100 percent.

An investigation was made of the vulcanization characteristics of guayule rubber through measurements of strain at 100 pounds per square inch. This showed that the guayule was similar to other rubbers, both natural and synthetic, in that the relationship between cure time and strain can be represented mathematically by the equation of a rectangular hyperbola of the form

$$(t - t_o)\ (E - E_{oo})\ k = 1,$$

where t is time of cure, and E is the elongation caused by a predetermined stress based on the cross section of the unstretched specimen. The symbols t_0 and E_{00} are constants determining the position of the asymptotes for the hyperbola; and k is a constant determining the curvature.

The vulcanization characteristics of guayule rubber were determined for four recipes yielding a wide range in the rate of cure. For test purposes, ACS #2 recipe was found to be best of those studied.

n. The Surety Rubber Company, Carrollton, Ohio. This company expressed an interest in testing deresinated guayule rubber in the fabrication of electricians' or linemans' gloves. Such gloves must be very durable and have high insulating qualities. Natural rubber is required for their manufacture. Gloves made from guayule rubber were compared with standard Hevea gloves. The reported results are shown in Table 11.

Table 11. Comparative Electrical Resistance of Guayule and Hevea Gloves (Surety Rubber Company)

Materials	Test Voltage	
	10,000	16,000
Hevea control	$7\frac{1}{2}$ - 8 M.A. leakage	10 - 12 M.A. leakage
Guayule No. 1	5 " " "	$7\frac{1}{2}$ " " "
Guayule No. 2	5 " " "	$7\frac{1}{2}$ " " "

Guayule No. 2 blew out at 20,000 volts.

Considerable enthusiasm was expressed over the low leakage values shown for guayule. The blow-out which occurred with the No. 2 glove was said to be probably due to insufficient acceleration in the compound formula. The desirability of conducting further tests was indicated.

o. W. J. Voit Rubber Corporation, Los Angeles, California. This organization manufactures basketballs, footballs, and other sporting goods and tire repair materials, including camelback.

A sample of shrub deresinated guayule rubber was tested as a replacement for washed smoked sheet Hevea (39% of the total hydrocarbon) in a camelback cushion compound. It was found that the guayule handled very well on the compounding mill, being similar to the plasticized washed sheets in this respect. The rate of cure slopes were equivalent and the stress-strain properties were similar to those of the washed sheets. The guayule had practically the same amount of tack immediately and 24 hours after milling.

Later, samples of both resinous and deresinated rubber were requested. These were prepared with an added non-staining antioxidant, as would be required in the manufacture of light-colored balls for sporting goods.

These samples were tested in a ball fabric friction compound. In this, smoked sheets were replaced by guayule on a direct hydrocarbon basis. The composition of the friction compound comprised 25 percent No. 1 Ribbed Smoked Sheet, 25 percent GR-S and 50 percent reclaim.

It was reported that the deresinated guayule replaced smoked sheets without a significant effect on stress-strain results. The resinous sample gave a compound having slightly lower modulus and tensile, and slightly higher elongation - but the differences were considered barely significant. The resinous guayule had the same hot tack as the smoked sheets; however, the deresinated sample showed reduced hot tack.

In the opinion of Mr. G. W. Miller, Chief Chemist, there would be no advantage in using deresinated guayule for compounds such as friction where subsequent fabrication requires good building tack.

p. American Society for Testing Materials, Philadelphia, Pa. A representative of the Salinas Laboratory was continuously associated with Committee D-11 (Rubber and Rubber-Like Materials) of the American Society for Testing Materials. Membership was held on eight sub-committees: X - Physical Testing; XI - Chemical Analysis; XII - Crude Natural Rubber; XIV - Abrasive and Tear Testing; XV - Life Tests for Rubber; XVII - Tests for Hardness, Set, and Creep; XXVI - Processibility; and XXVII - Tests for Resilience. The Salinas representative was Chairman of Sub-committee XXVI.

Active participation in the ASTM has aided the laboratory materially. It has enabled the personnel to keep abreast of the activities of industry, has aided in acquainting industry with some of the accomplishments of the laboratory, and has been directly responsible for much of the cooperative work done by various industrial organizations.

The majority of the improvements made in physical testing techniques and testing equipment have resulted from benefit of discussions of the problems involved in the above-mentioned ASTM sub-committees. The more important of these improvements concerned the determination and effects of moisture in crude rubber and rubber compounds, determination of dirt in crude rubber, compounding and curing procedures, and stress-strain testing techniques.

q. Miscellaneous Cooperation. In addition to the interest shown by industry in the quality appraisal of guayule rubber, some interest also developed in connection with the testing of byproducts of guayule processing.

The Texas Agricultural Experiment Station conducted cattle and sheep feeding trials with samples of guayule leaves as recovered from the parboiling step of the pebble milling process. The leaves contained an average of about 9.4 percent protein. However, the livestock refused to eat the leaves even when mixed with other feed. Thus, it was reported that guayule leaves were not considered sufficiently palatable to make them of practical value as a livestock feed.

Several firms and individuals were supplied with samples of guayule resins obtained in connection with worm rubber deresination. Armour & Co.,

Chicago, Illinois, requested samples with a view to the investigation of partheniol as an organic intermediate. The Harvel Research Corporation, Irvington, New Jersey, showed an unusual interest in the resins and expressed the belief that this byproduct had commercial possibilities. Information as to large scale availability and price in ton lots was requested by this organization. Although several samples (one of 5 gallons) were forwarded at different times on request, no report of tests was received. The Harvel Research Corporation is a research laboratory which looks into the development of potentialities of various materials, and appears to be associated with the Irvington Varnish and Insulation Co., also of Irvington, New Jersey.

Mr. H. S. Carter, RFD #4, New London, Conn.; Mr. George W. Sherman, Box 630, Akron, Ohio; and Dr. E. W. Engel of Industrial Tape Corporation, New Brunswick, New Jersey, were each furnished small samples of resins on request. No reports were received.

3. Low Temperature Evaluation

During the latter part of 1948 Mr. John Caswell, who was then Assistant Chief of the Rubber Division, Office of Domestic Commerce, Department of Commerce, became interested in the possible value of guayule under Arctic conditions, and suggested that appropriate studies be undertaken. The theory was that guayule rubber, particularly as extracted from young shrub, was of comparatively low molecular weight and that, accordingly, it would have a lower freeze point than Hevea rubber. The Navy was interested in service conditions as low as -35° F., and other services go as low as -80° F. Work on this problem was undertaken by the Government Laboratories, University of Akron; the National Bureau of Stardards; and the U. S. Naval Rubber Laboratory at Mare Island, Calif. Rubber products for which good low temperature properties are vital include tires, gaskets, engine mountings, linings in self-sealing gasoline tanks, etc.

Typical 3- to 4-year-old shrub was used for preparation of the rubber samples. The plant material was fractionated before milling into tips, branches, and roots, in order to accentuate molecular weight differences within the plant as much as possible. In addition, whole shrub rubber, both resinous and deresinated, were included. Guayule latex rubber was also submitted for these tests. Rubber extracted from the separate plant fractions was not deresinated. Differences in molecular weight among the different samples were not as great as had been anticipated. The range in molecular weight, as determined by the solution viscosity method, was from 122,000 for tip rubber to 146,000 for deresinated rubber from whole shrub. (These figures are of relative significance only and cannot be compared with figures commonly reported for Hevea and other rubbers.) Differences in resin content were superimposed upon differences in molecular weight in evaluation of low temperature characteristics. Controls of natural rubber, GR-S and polybutadiene were included in the tests. Both gum and carbon black type vulcanizates were prepared.

The Government Laboratories reported, as shown in Table 12, that the freeze point value for rubber obtained from the root fraction was the lowest.

Table 12. Freezing Point Values for Guayule Rubber in Relation to Fraction of Shrub

Source of Rubber	Freezing Point (Gehman) Minus ° C.
Whole shrub, resinous	58
Whole shrub, deresinated	56
Tips of shrub	57
Branches of shrub	57
Roots of shrub	61
Latex	57
Hevea	56

However, molecular weights apparently did not influence the low temperature properties. Vulcanizates of the deresinated guayule and Hevea rubber had identical freeze points. It was therefore assumed that the resin content of the guayule influences the low temperature properties more than does the molecular weight. This is in accord with a statement made by Dr. Bekkedahl, of the National Bureau of Standards, to the effect that in dealing with linear polymers such as natural rubber no marked change in physical properties correlated with molecular weight were observed until the molecular weight was reduced to about 10,000.

Tests made at the U. S. Naval Rubber Laboratory on compression set of resinous guayule rubber in comparison with Hevea rubber led to the conclusion that the guayule has no better low temperature resistance than Hevea rubber, and that neither is as good as GR-S compounded for low temperature service.

4. Truck and Passenger Car Tire Tests

Research contracts for the construction of experimental truck and passenger car tires, using deresinated guayule rubber, were negotiated by the Synthetic Rubber Division (formerly the Office of Rubber Reserve), Reconstruction Finance Corporation, with three tire manufacturers. The Firestone Tire & Rubber Co., Akron, Ohio, the Goodyear Tire & Rubber Co., Akron, Ohio, and the Armstrong Rubber Co., West Haven, Conn., were included in this program. The objective was to determine quality and serviceability of deresinated guayule rubber, as developed and improved by the Bureau of Agricultural and Industrial Chemistry, for the carcass stock of tires in comparison with Hevea rubber. Evaluation of the performance of guayule in heavy-duty truck tires was of special importance, since natural rubber is essential for this critical purpose because of the heat build-up factor in the carcasses of

large-size transport tires. Approximately 4,000 pounds of deresinated guayule rubber were prepared for this purpose.

The first set of tires was fabricated by the Firestone Tire & Rubber Co. These were heavy-duty truck tires, size 9:00 x 20, 10-ply rating. Three different carcass compositions, and three tires of each, were used for comparison with three standard tires with 100 percent Hevea carcass. The different carcass stocks included a blend of 45 parts of guayule with 55 parts of GR-S synthetic, and a similar blend of Hevea with synthetic, in addition to the 100 percent guayule carcass. Treads in all cases were "cold" GR-S. Road tests were conducted by the Government Tire Test Fleet at Camp Bullis, San Antonio, Texas. Tire loads, using gravel ballast on the trucks, were 145 percent of the recommended maximum to increase the severity of the test.

The results of the first truck tire test, conducted during the summer and fall of 1951, were of outstanding significance. It was shown that the 100 percent guayule and 100 percent Hevea carcass constructions were equal in durability; one tire of each was still running at 50,900 miles when the test was discontinued. Based on the average miles to failure of the other two tires of each construction, guayule might be considered slightly superior to Hevea. Both guayule and Hevea blends with synthetic were inferior to the 100 percent natural rubber constructions, but were equal to one another in durability, based on average miles to failure.

The tires were fitted with thermocouple wires which permitted measurements of temperature to indicate relative heat build-up. The tires containing synthetic blends had the highest running temperature, while the 100 percent Hevea and 100 percent guayule tires were essentially the same. The GR-S treads on the 100 percent natural rubber carcasses were approximately equal in resistance to cracking on both guayule and Hevea tires, with a slight advantage in favor of guayule.

A summarized tabulation of the road test data is shown in Table 13.

A second heavy-duty truck tire test, using tires fabricated by the Armstrong Rubber Co., and following the above-described pattern was inconclusive. For unknown reasons, all tires containing guayule rubber failed because of tread separation at extremely low mileages; in one case at only 576 miles. This test was scheduled to be repeated and a second batch of 1500 pounds of deresinated guayule rubber was furnished for the purpose.

Table 13. Summary of Results of Road Tests on Heavy-Duty Truck Tires Using Deresinated Guayule Rubber in Comparison With Hevea Rubber

Composition of tire carcass	Tread Wear Rating	Tread Cracks to Fabric: Longest	Tread Cracks to Fabric: Total	Carcass Diameter Increment	Average Tire Temperature	Miles to Failure	Remarks
		Inches	Inches	%	°F.		
Hevea, 100 percent							
No. 1		4	12		221	31,976	Body break
No. 2	100	2	5	3.01	221	50,900	Still running at end of test
No. 3		4	16		225	34,983	Tread separation
Hevea/GR-S (55/45 blend)							
No. 1		5	8		227	20,574	Body break
No. 2	98	4	16	3.62	227	24,615	Body break
No. 3		4	12		232	24,244	Body break
Guayule/GR-S (55/45 blend)							
No. 1		5	31		232	22,814	Tread crack separation
No. 2	96	1	1	3.52	232	14,446	Body break
No. 3		4	31		233	31,788	Body break
Guayule, 100 percent							
No. 1		3	11		216	34,720	Body break
No. 2	101	4	10	2.89	221	50,900	Still running at end of test.
No. 3		4	15		227	38,743	Body break

Project	"BZ"
Construction	Rayon - highway tread
Size	9.00-20, 10-ply rating
Wheel Position	Rear alternated
Load	5,000 pounds
Inflation	65 pounds
Route	92% pavement - 8% gravel first 7,000 miles 100% pavement thereafter
Speed	45 M.P.H. pavement - 30 M.P.H. gravel

Average Temperature	71° F.
Maximum Temperature	104° F.
Minimum Temperature	27° F.
Duration of Test	92 days
Average wet miles per Tire	2,294
Average total miles per tire	31,720

Guayule Rubber in Comparison With Hevea Rubber

Miles to Failure	Remarks
31,976	Body break
50,900	Still running at end of test
34,983	Tread separation
20,574	Body break
24,615	Body break
24,244	Body break
22,814	Tread crack separation
14,446	Body break
31,788	Body break
34,720	Body break
50,900	Still running at end of test.
33,743	Body break

ıge Temperature	71° F.
ıum Temperature	104° F.
ıum Temperature	27° F.
:ion of Test	92 days
ıge wet miles per Tire	2,294
ıge total miles per tire	31,720

Passenger car tires, 7:00 x 15, 4-ply rayon cord, were manufactured by the Goodyear Tire & Rubber Co. and tested by the Government Tire Test Fleet in the spring of 1952. The same experimental plan was followed as in the case of the truck tires. Unfortunately, however, any attempt to evaluate carcass durability would probably not be valid because most of the tires were worn to fabric before the test was completed. Only two tires, one of the 100 percent guayule group and one of the Hevea/GR-S blends, suffered carcass failure. The "cold" GR-S treads were stated to have been more resistant to treadwear on the Hevea carcasses at the time the testing was discontinued (23,201 miles).

5. Airplane Tire Tests

The U. S. Air Force, Wright-Patterson Air Force Base became actively interested in conducting tests with airplane tires, following the excellent showing made by deresinated guayule rubber in the first truck tire test. Intensive efforts are being made by the Air Force to relieve this country's dependence upon imported Hevea rubber, since airplane tires must be fabricated entirely of natural rubber. After considering the problem of testing the guayule rubber with a number of airplane tire manufacturers, a contract was made with the Frank G. Schenuit Rubber Co., Baltimore, Maryland, for construction of experimental tires. A 2500-pound lot of deresinated guayule rubber was supplied for the purpose in February 1953.

6. General Appraisal

Letters of inquiry were sent to former or current users of guayule rubber (customers of the Intercontinental Rubber Co.) in order to obtain the benefit of advice and general experience of the rubber industry. This was considered to be of value in guiding investigations on the development of guayule rubber as a domestic source of natural rubber. The following questions were asked: Does resinous guayule rubber, such as produced in Mexico, meet a special or critical need or has its use been governed mainly by price or other considerations in relation to Hevea? Does guayule have any known use for which it is especially well suited or even superior to Hevea? What physical properties of resinous guayule are considered to be most important? Would such properties be improved or rendered less desirable by deresination? Would a high grade deresinated product (equal in quality to Hevea for tire carcass stock) have any preferred use assuming price equality with Hevea? Does the deterioration which takes place on storage of the commercially available resinous rubber constitute a serious problem?

Companies to which the above-mentioned letters of inquiry were addressed are listed in Table 14.

The largest user of guayule rubber has traditionally been the B. F. Goodrich Company. It was reported that at one time a so-called masterbatch was prepared from the guayule rubber. This consists of a very concentrated mixture of compounding ingredients with a limited amount of rubber which can subsequently be more readily incorporated in fixed proportions with large batches of rubber than can the separate compounding ingredients. A soft and easily processible rubber (such as resinous guayule) is obviously desirable for the masterbatch. Guayule was mentioned as being required by Government specification for one product (not identified).

A well-known wartime use of guayule rubber was for the fabrication of the inner sealing liner for bulletproof or self-sealing gasoline tanks. However, guayule is regarded as having no special merit for this purpose, but was used mainly to conserve critical supplies of Hevea during World War II.

The Firestone Tire & Rubber Company regards resinous guayule rubber as serving the dual purpose of being a source of rubber hydrocarbon as well as a softener. It can be used, for example, in a tire carcass stock and the amount adjusted, normally up to about 4 percent of the total rubber, to give the desired workability of such a stock. Nevertheless, its use was considered as being dependent upon price in relation to Hevea rubber. Thus, if guayule were priced sufficiently lower than Hevea, it could be used in small amounts at a saving in cost without a loss of quality. The opinion was expressed that deresinated guayule (as developed at Salinas) would have about the same characteristics as the regular market grades of Hevea.

The superior tack and plasticity or ready workability was frequently mentioned by industrial users as a property of guayule rubber which is desirable, such as in the manufacture of friction stocks and belting, extrusion stocks, tires, hose, and miscellaneous molded goods. The most important

Table 14. Users of Commercial Mexican Resinous Guayule Rubber During Years 1950-51
(Information furnished by courtesy of Intercontinental Rubber Co., New York)

Name	Use
Cambridge Rubber Co., Cambridge, Mass.	Footwear
Cornish Wire Co., Williamstown, Mass.	Wire insulation
Eagle Rubber Co., Ashland, Ohio	Rubber balls and toys
Firestone Tire & Rubber Co., Akron, O.	Assume fuel cells and possibly tire carcass compounds
Gates Rubber Co., Denver, Colo.	Camelback, extruded and friction compounds
General Tire & Rubber Co., Akron, O.	Assume friction compounds and camelback
B. F. Goodrich Co., Akron, O.	Fuel cells, heels and soles
Goodyear Tire & Rubber Co., Akron, O.	Unknown
LaCrosse Rubber Mills Div., LaCrosse, Ind.	Footwear
Home Rubber Co., Trenton, N.J.	Assume friction compounds and extruded specialties
Hood Rubber Co., Watertown, Mass.	Footwear
Manhattan Rubber Mfg., Div. of Raybestos-Manhattan, Inc., Passaic, N.J.	Assume friction and extruded specialties
Mansfield Tire & Rubber Co., Mansfield, O.	Assume tire carcass compounds and possibly camelback
Mohawk Rubber Co., Akron, O.	Camelback
New York Rubber Corp., Beacon, N.Y.	Friction and extruded stocks
Okonite Company, Passaic, N.J.	Insulated wire and friction tape
Paragon Rubber Co., Easthampton, Mass.	Toys, novelties, molded specialties
Pennsylvania Rubber Co., Jeanette, Pa.	Unknown
Seiberling Latex Products, Barberton, Ohio	Ball and toy specialties
Seiberling Rubber Co., Akron, O.	Unknown
Tyer Rubber Co., Andover, Mass.	Footwear, mechanical specialties
United States Rubber Co., N.Y. City	Footwear, fuel cells

physical property of resinous guayule was thought by some to be the effect of producing building tack in very high synthetic carcass compounds. One organization, the General Tire & Rubber Co., stated that if the quality and price of deresinated guayule were equal to Hevea, the guayule would have a preferred use because of better handling characteristics which would be found in stock processing and tire building operations. There is, however, a limit to the amount of resinous guayule that can be used because of adverse effects on other physical properties.

Price is, of course, a primary consideration though not always the determining factor. Opinion was expressed that guayule should not sell for more than about 75 to 80 percent of the price prevailing on No. 1 smoked sheet. In general, there appears at the present time to be only a few preferred uses for resinous guayule rubber in which price is not an important factor.

The Goodyear Tire & Rubber Co., for example, stated that their usage of resinous guayule has been very limited and uneconomical, and that from their viewpoint this rubber had no special or critical application. On the other hand, the Seiberling Rubber Company has used small quantities of resinous guayule rubber for a number of years to meet a special need (unknown) in which the price is not a factor. The characteristic in which they are interested is a function of the resinous component and they are, therefore, not interested in a deresinated product. Also, the Hood Rubber Company (a division of the B. F. Goodrich Co.) indicated that they use small amounts of resinous guayule and expect to continue its use in a specialized friction stock which is used for in-soles in canvas shoes. They have been able to obtain better results from guayule than with Hevea rubbers, even when used in combination with the ordinary resins used in rubber compounding.

Raybestos-Manhattan, Inc., manufacturers of mechanical goods (including brake linings, clutch facings and packings) have used small quantities of resinous guayule continuously for at least 35 years. Price has not been the determining factor in their usage, but rather the special properties of plasticity or ready workability which guayule imparts to stocks containing it.

Some companies bought guayule rubber during the period Hevea rubber restriction since guayule was on the "free" list. One company, the Eagle Rubber Co., manufacturer of toys and novelties (balloons, inflated balls and toys) mentioned that they had no previous experience with this rubber until restrictions were placed on Hevea rubber, and that they did not have good results in its use because of difficulty in getting a good cure. Likewise, previous experience of the Okonite Co., manufacturers of insulated wire and cable, friction and rubber tape, weather stripping, etc., was limited to the use of guayule during times when other types of natural rubber were not available or not permitted by law. This company stated that on the basis of laboratory tests, rubber splicing tape in which deresinated guayule rubber was used showed lower electrical, tensile and fusion properties when compared to rubber tape made with either fine Para or smoked sheet. However, commercial friction and cable tapes made with deresinated guayule rubber, alone or in combination with natural rubber reclaims, showed good results but not better than fine Para or smoked sheet rubbers.

More specific information on guayule uses has been difficult to obtain. Many organizations are naturally reluctant to reveal what they consider to be in the nature of a trade secret. This is especially true of compounding formulations.

Concerning the problem of deterioration of resinous guayule rubber during storage, it was evident that such rubber should be used promptly in order to avoid difficulty.

Deresination was regarded as a means of up-grading guayule to the point where it would have characteristics similar to those of the regular market grades of Hevea, especially in view of the results of the Firestone truck tire tests, and impressions gained from samples of deresinated rubber recently submitted for examination and testing.

V. PUBLICATIONS AND PATENTS

A. Publications

Papers

1. Banigan, T. F., Jr. Differential Migration of Rubber by Reversed-Phase Partition Chromatography. Ind. Eng. Chem., 45, 572 (1953).

2. Banigan, T. F., Jr. Diffusion Phenomena in Solvent Deresination of Guayule Rubber. Science, 117, 249 (1953).

3. Banigan, T. F., Jr., Meeks, J. W., and Planck, R. W. The Distribution of Waxes in Guayule. Bot. Gaz., 112, (6), 231 (1951).

4. Chubb, R. L., Taylor, E. C., and Feustel, I. C. Deresination as a Means of Improving the Quality of Guayule Rubber. I. Shrub Deresination. India Rubber World, 123, 557 (1951).

5. Clark, F. E. Domestic Natural Rubbers. Chem. Eng. News, 26, 296 (1948).

6. Clark, F. E., Banigan, T. F., Jr., Meeks, J. W., and Feustel, I. C. High Quality Rubber by Acetone Deresination of Guayule. Ind. Eng. Chem., 45, 572 (1953).

7. Feustel, I. C., and Clark, F. E. Opportunities to Grow Our Own Rubber. U. S. Dept. of Agric. Yearbook of Agriculture, 367 (1950-51).

8. Gowans, W. J. Preparing Crude Rubber Test Specimens for Oxygen-Absorption Measurements. Anal. Chem., 24, 1648 (1952).

9. Gowans, W. J., and Clark, F. E. Determination of Rubber Hydrocarbon by a Modified Bromination Method. Anal. Chem., 24, 529 (1952).

10. Jones, E. P. Recovery of Rubber Latex from Guayule Shrub. Ind. Eng. Chem., 40, 864 (1948).

11. Meeks, J. W., Banigan, T. F., Jr., and Planck, R. W. A Low-Molecular-Weight Fraction of Guayule Rubber. India Rubber World, 122, 301 (1950).

12. Meeks, J. W., and Feustel, I. C. The Molecular Weight of Rubber as Influenced by Extraction and Processing Treatments. India Rubber World, 125, 187 (1951).

13. Taylor, K. W. Guayule--An American Source of Rubber. Eco. Bot., 5(3), 255 (1951).

14. Taylor, K. W., and Chubb, R. L. Development of Pilot Plant Control for Milling Guayule Shrub. Ind. Eng. Chem., 44, 883 (1952).

15. Taylor, K. W., and Chubb, R. L. Rubber Recovery from Freshly Harvested Guayule. Ind. Eng. Chem., 44, 879 (1952).

6. Taylor, R. H. Fixtures Aid in Sharpening Dies to Cut Rubber Tensile Test Specimens. India Rubber World, 123, 441 (1951).

7. Taylor, R. H., and Ball, W. P. Temperature Measurements in the Mooney Viscometer. ASTM Bulletin No. 176, 60 (1951).

8. Taylor, R. H., and Veith, A. G. Mooney Viscosity Measurements in Determining Processibility of Technically Classified Rubbers. ASTM Special Technical Publication No. 136 (50th Anniv. Pub.) (1953).

pers in Press

1. Banigan, T. F., Jr., and Meeks, J. W. Isolation of Palmitic, Stearic, and Linoleic Acids from Guayule Resin.

2. Clark, F. E. The Determination of Dirt in Raw Guayule Rubber.

3. Gowans, W. J., and Clark, F. E. Improved Aging Characteristics of Raw Guayule Rubber.

4. Meeks, J. W., Crook, R. V., Pardo, C. E., Jr., and Clark, F. E. An Improved Method of Determining Rubber Hydrocarbon in Rubber-Bearing Plants.

5. Taylor, R. H., Ball, W. P., and Clark, F. E. Effect of Moisture on Curing Characteristics of Rubber.

stracts

1. Aging Characteristics of Crude Guayule Rubber. India Rubber World, 127, 658 (1953).

2. An Improved Method of Determining Rubber Hydrocarbon in Rubber-Bearing Plants. India Rubber World, 127, 658 (1953).

3. Determination of Rubber Hydrocarbon by an Improved Bromination Procedure. India Rubber World, 123, 580 (1951).

4. Mooney Viscosity Measurements of Technically Classified Rubbers. Rubber Age, 71, 238 (1952).

5. Natural Rubber From Domestic Plants. The Vortex, 10, 548 (1949).

6. Preparing Crude Rubber Test Specimens for Oxygen-Absorption Measurements. Anal. Chem., 24, 1648 (1952).

B. Patents

tents Granted

1. Banigan, T. F., Jr., Meeks, J. W., and Planck, R. W. Process of Isolating Resins from Guayule Extract. U. S. Patent 2,549,763 (1951).

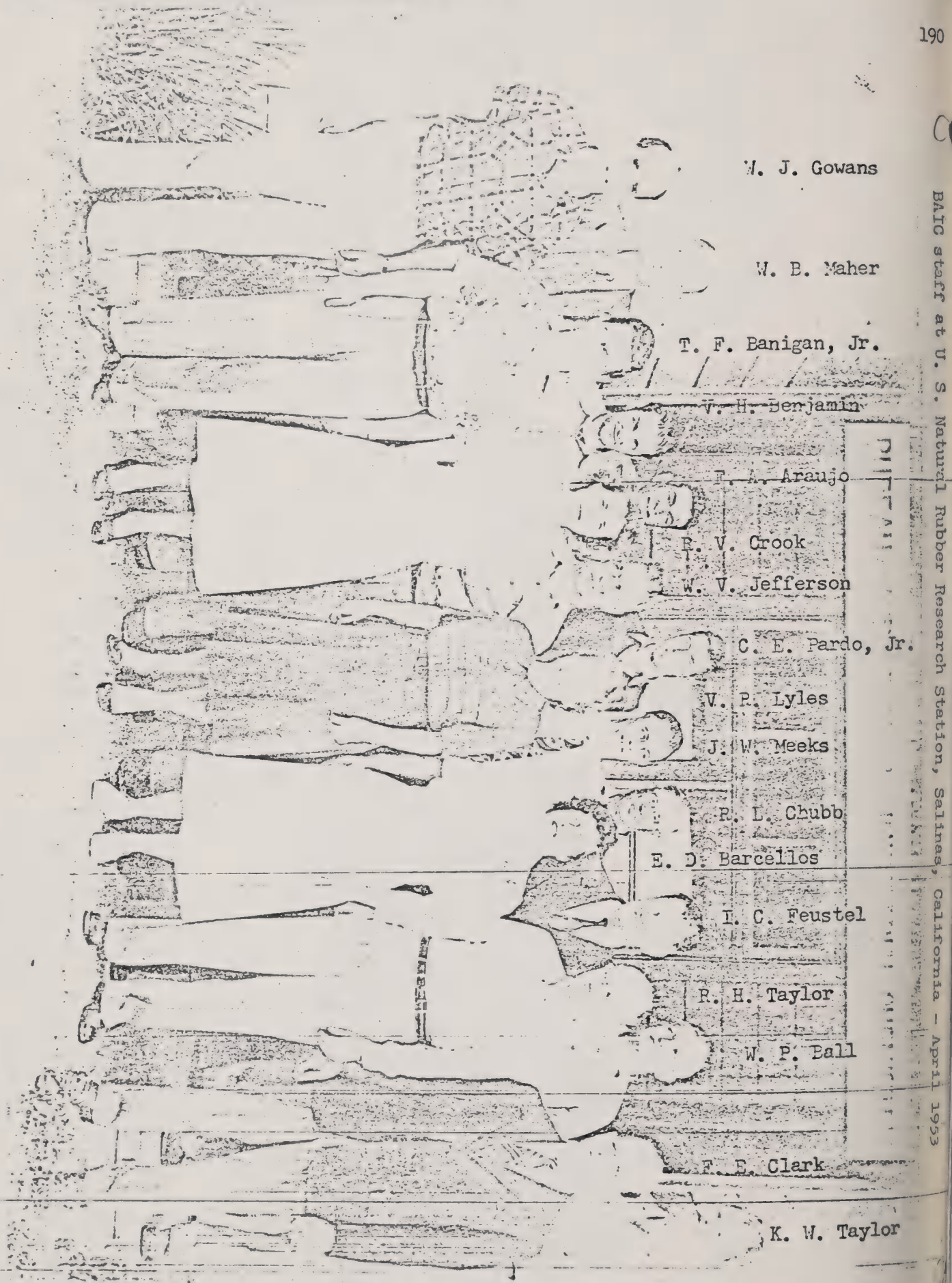
2. Jones, E. P. Process of Concentrating Aqueous Rubber by Centrifuging. U. S. Patent 2,475,141 (1949).

3. Jones, E. P. Recovering Rubber From Guayule Shrub. U. S. Patent 2,434,412 (1948).

4. Meeks, J. W., Banigan, T. F., Jr., and Planck, R. W. Process for Recovering Parthenyl Cinnamate and Essential Oils from Guayule Resin. U. S. Patent 2,572,046 (1950).

Patent Pending

1. Clark, F. E., and Feustel, I. C. Method of Treating Rubber Obtained from Rubber-Bearing Plants. U. S. Patent Application Ser. No. 256,356.



BAIC staff at U. S. Natural Rubber Research Station, Salinas, California - April 1953

Entrance at U. S. Natural Rubber Research Station, Salinas, Calif. (Hartnell A & M Junior College in background)

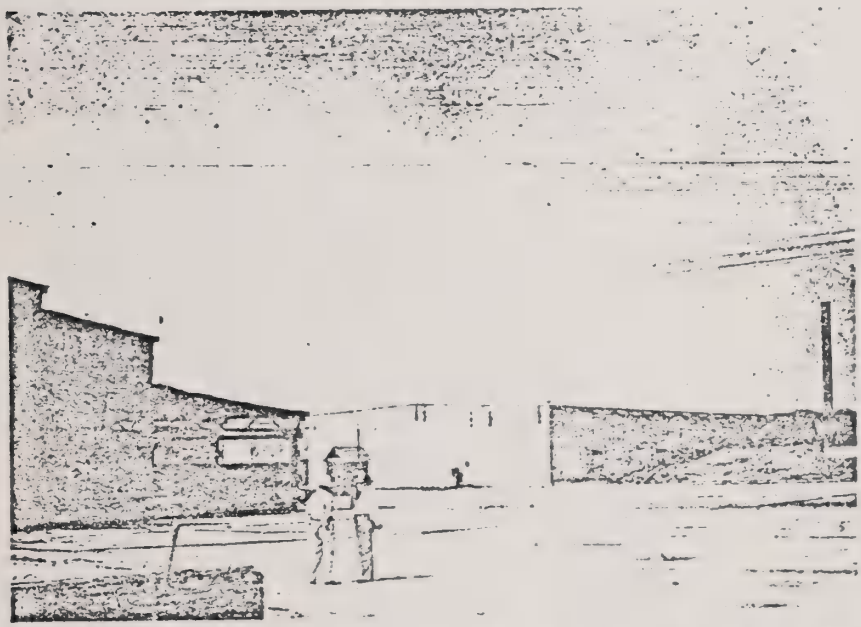
Dr. H. M. Tysdal, Project Leader, BPIS&AE (left) and Dr. I. C. Feustel, Head BAIC Unit, inspect a field of guayule shrub at Spence Field, Salinas, Calif.

A "guayulero" and his burro in Durango, Mexico bring a load of guayule to the baling camp for transport to the mill of the Continental Mexican Rubber Company at Torreon, Mexico. Note the water keg on the burro.

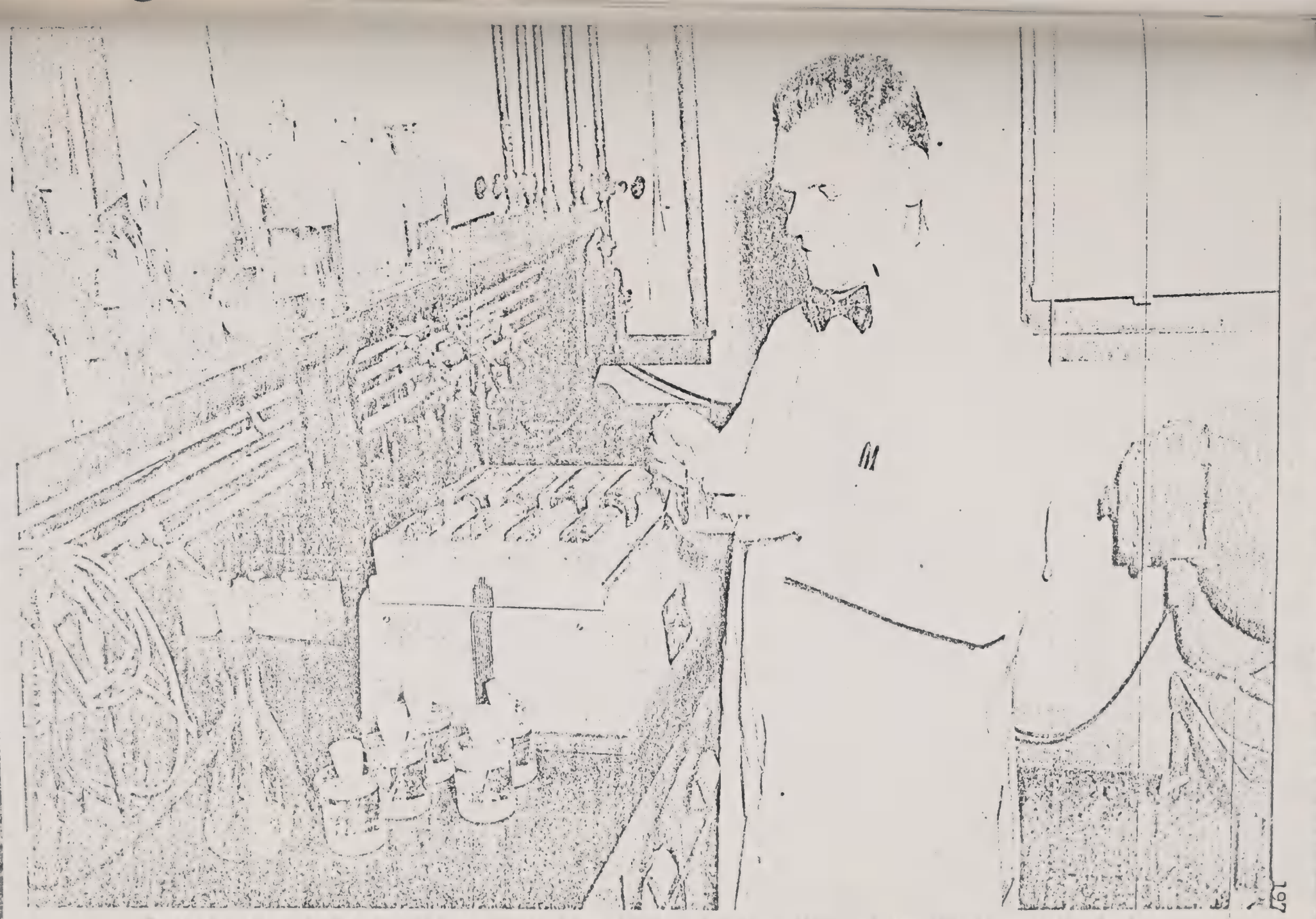
Typical guayule range in Durango, Mexico. Bob Ross, Manager, Continental Mexican Rubber Company beyond the ocotillo in the foreground.

Weighing in wild guayule collected from the ranges of Durango, Mexico, for milling by the Continental Mexican Rubber Company.

A Mexican laborer spreading guayule bagasse in the evaporation ponds at the site of the Continental Mexican Rubber Company, Torreon, Coahuila, Mexico.

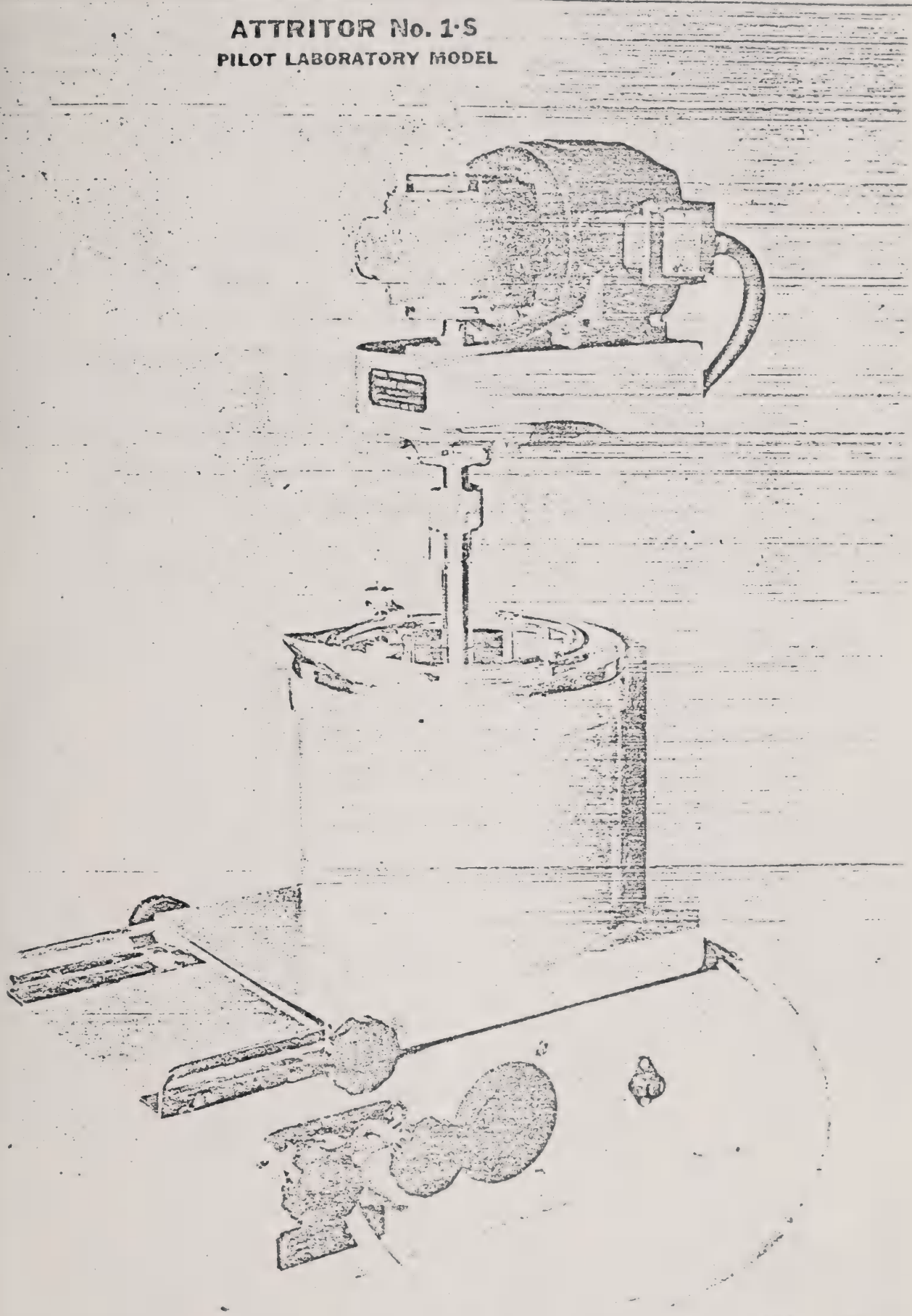


Carl F. Speh, Assistant Chief of Bureau, and Bob Ross, Manager, Continental Mexican Rubber Company.

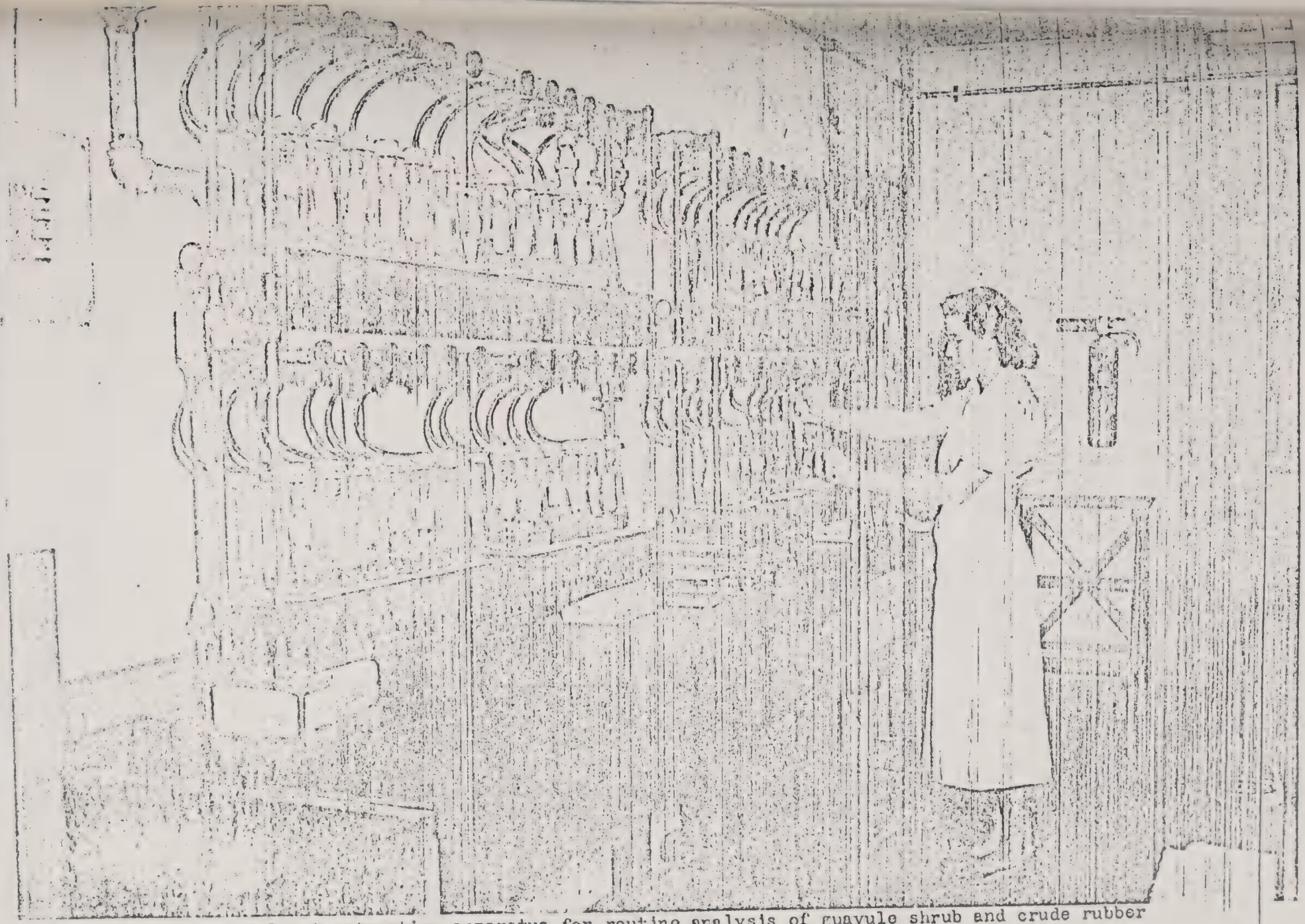


Demonstration of the new shaker method for determination of rubber hydrocarbon in guayule shrub.

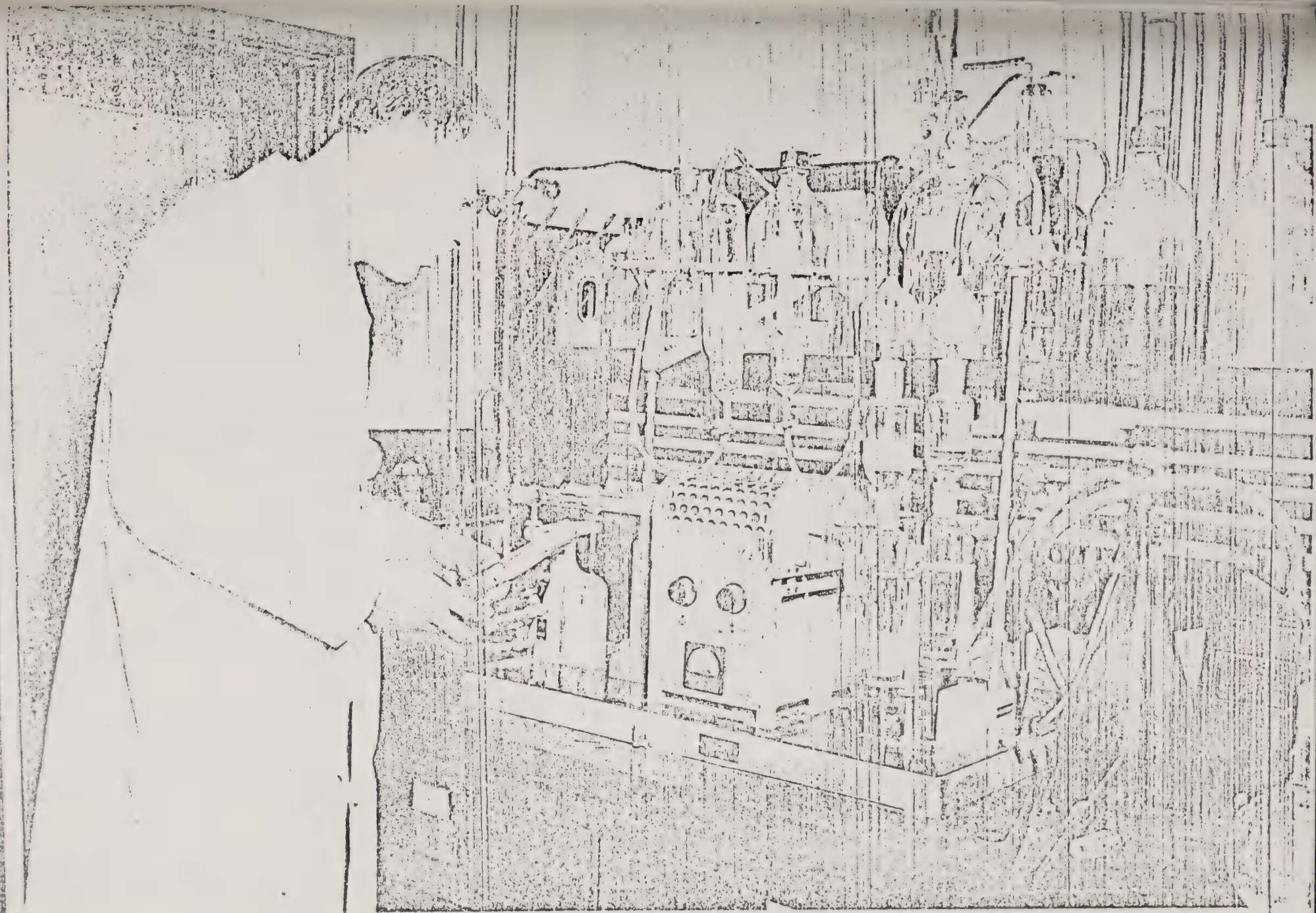
Apparatus for determination of molecular weight of guayule rubber



The attritor---a new laboratory type pebble mill for experimental milling of guayule shrub

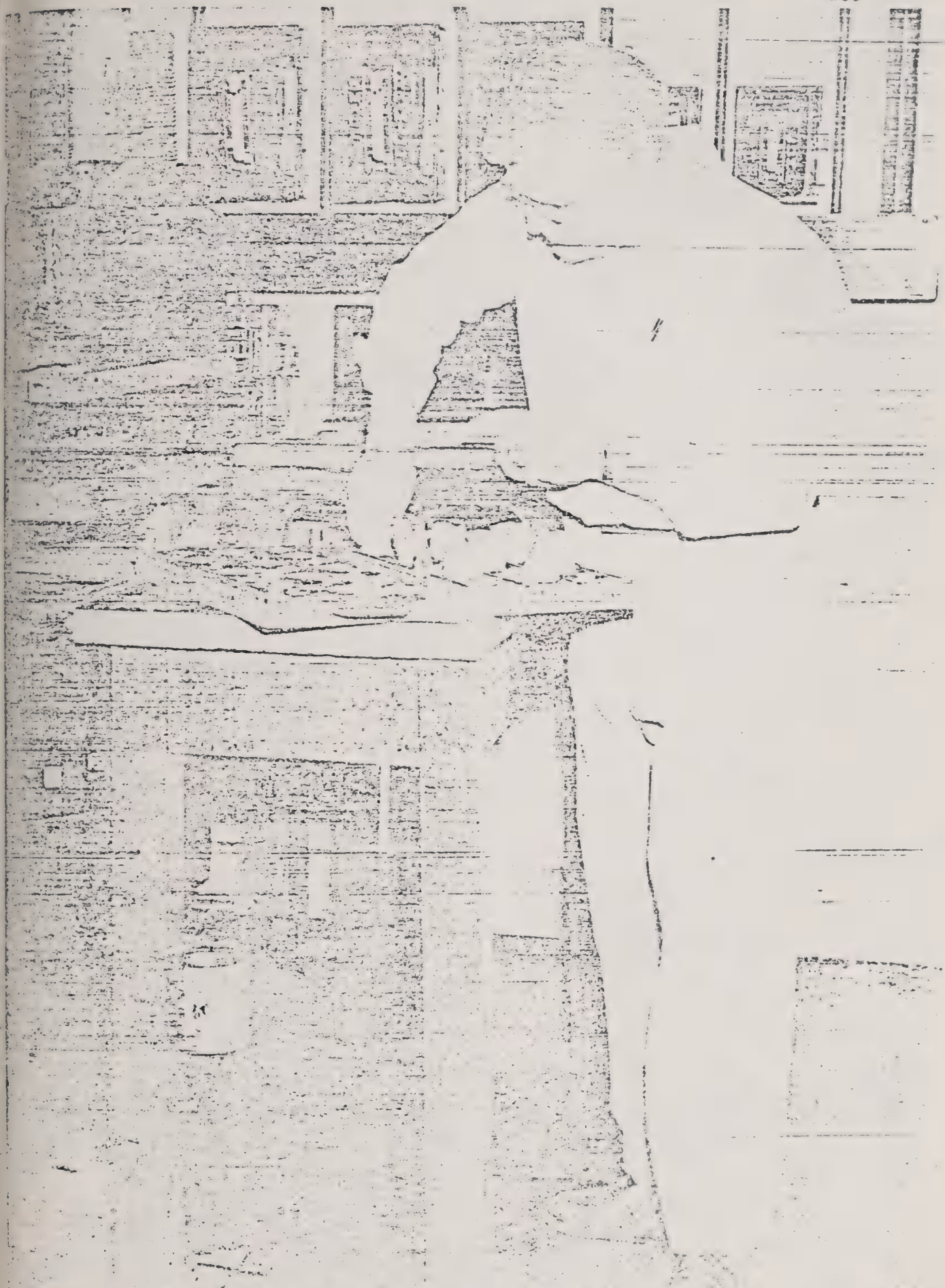


Solvent extraction apparatus for routine analysis of guayule shrub and crude rubber

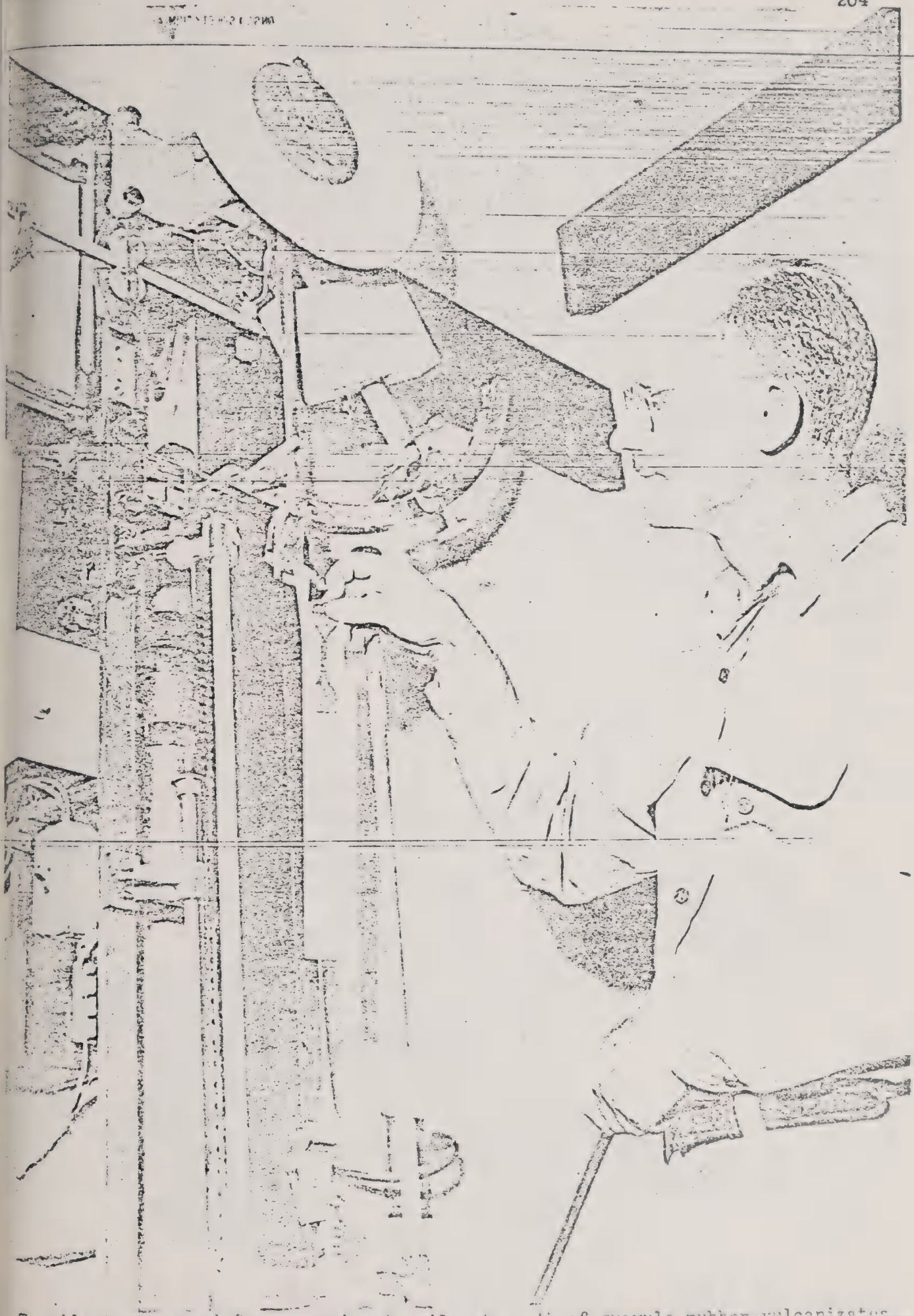


Apparatus used for determining composition of rubber hydrocarbon bromides

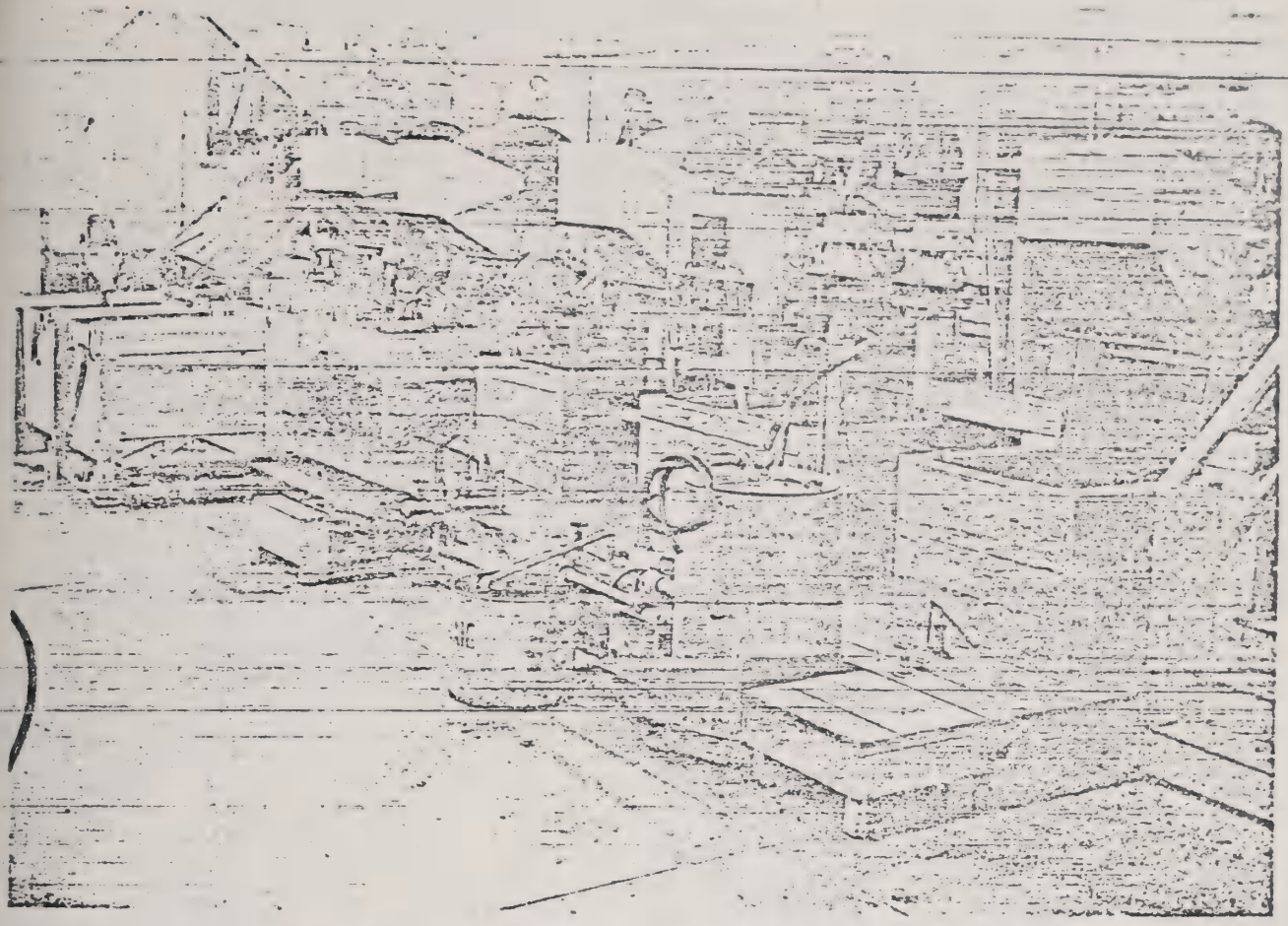
Oxygen absorption equipment used for accelerated aging tests on guayule rubber



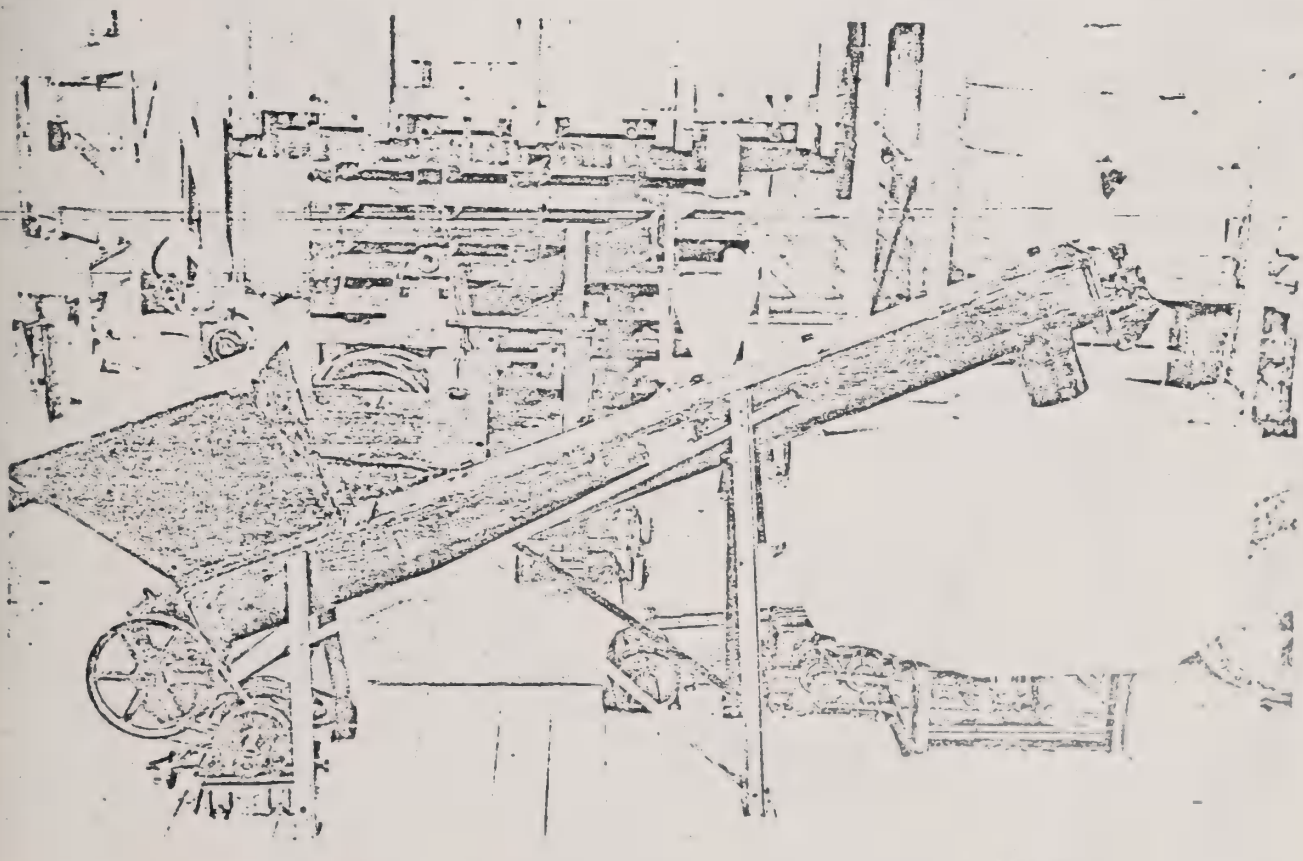
Loading a ball mold with compounded
guayule rubber for vulcanization



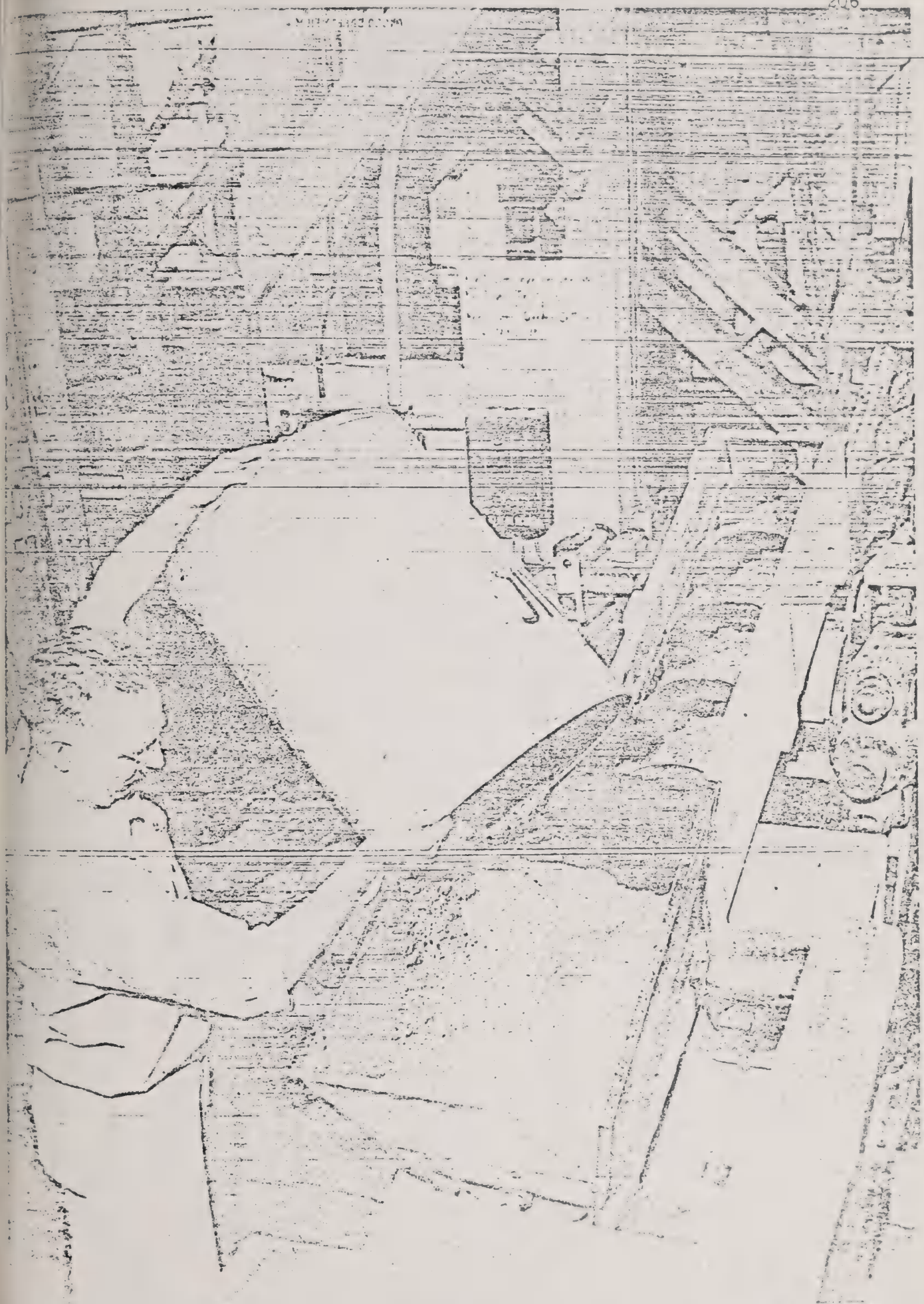
Tensile tester used for measuring tensile strength of guayule rubber vulcanizates.



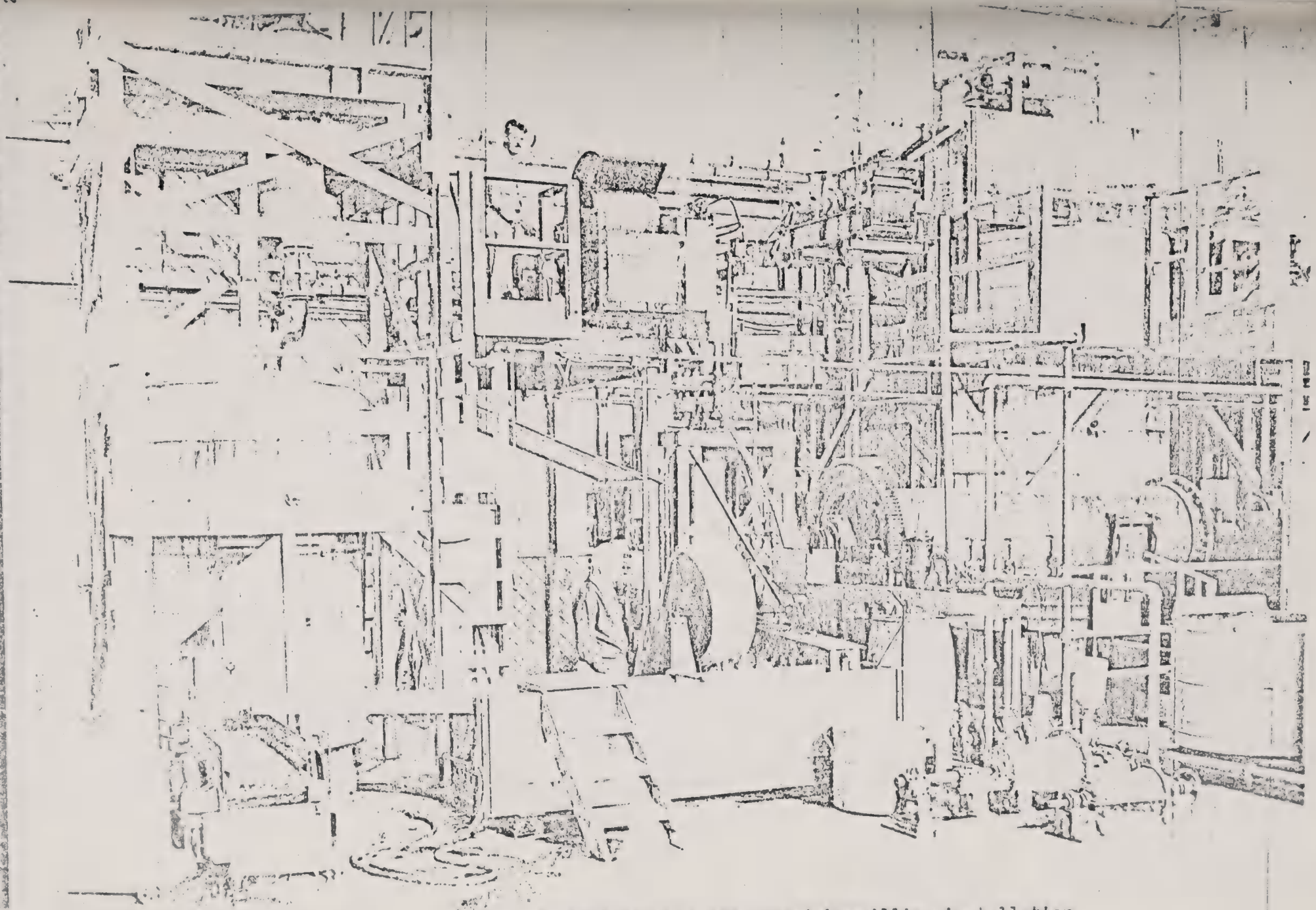
Battery of batch pebble mills used for controlled milling studies



Guayule shrub sample divider for analysis of material as prepared for milling

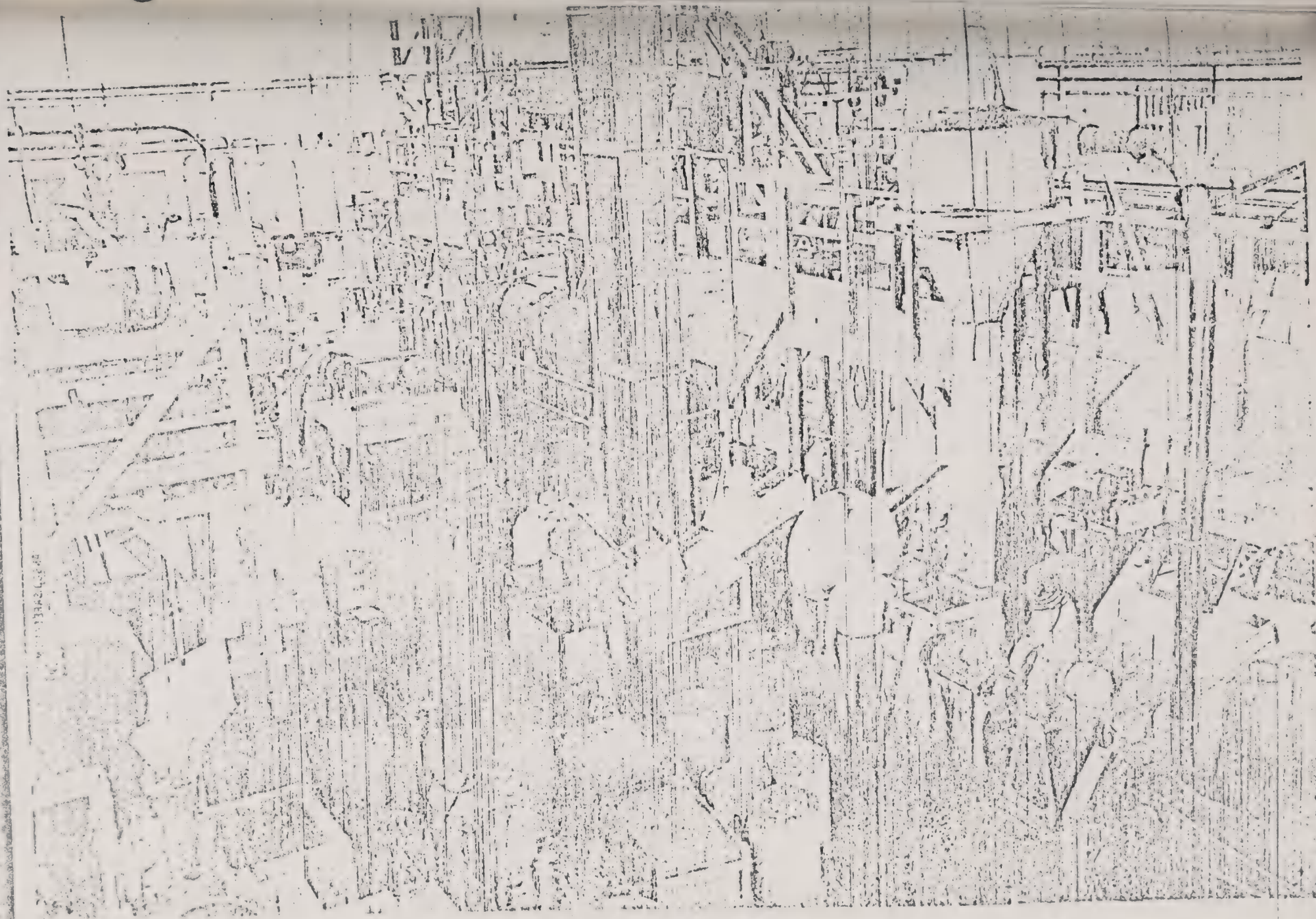


ontinuous feeder to roll crusher for crushing guayule shrub in preparation for milling

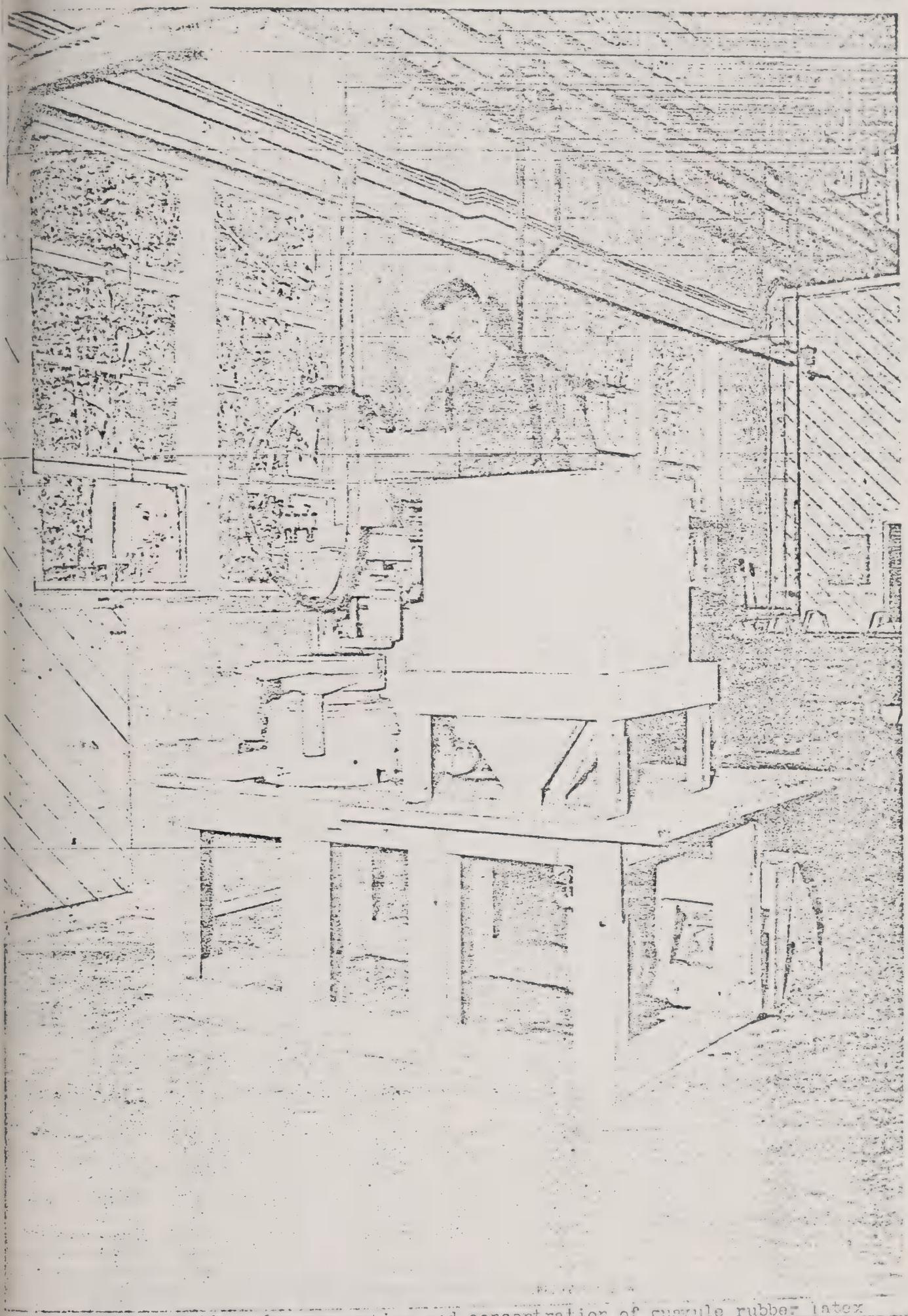


View of pilot plant continuous tube milling installation

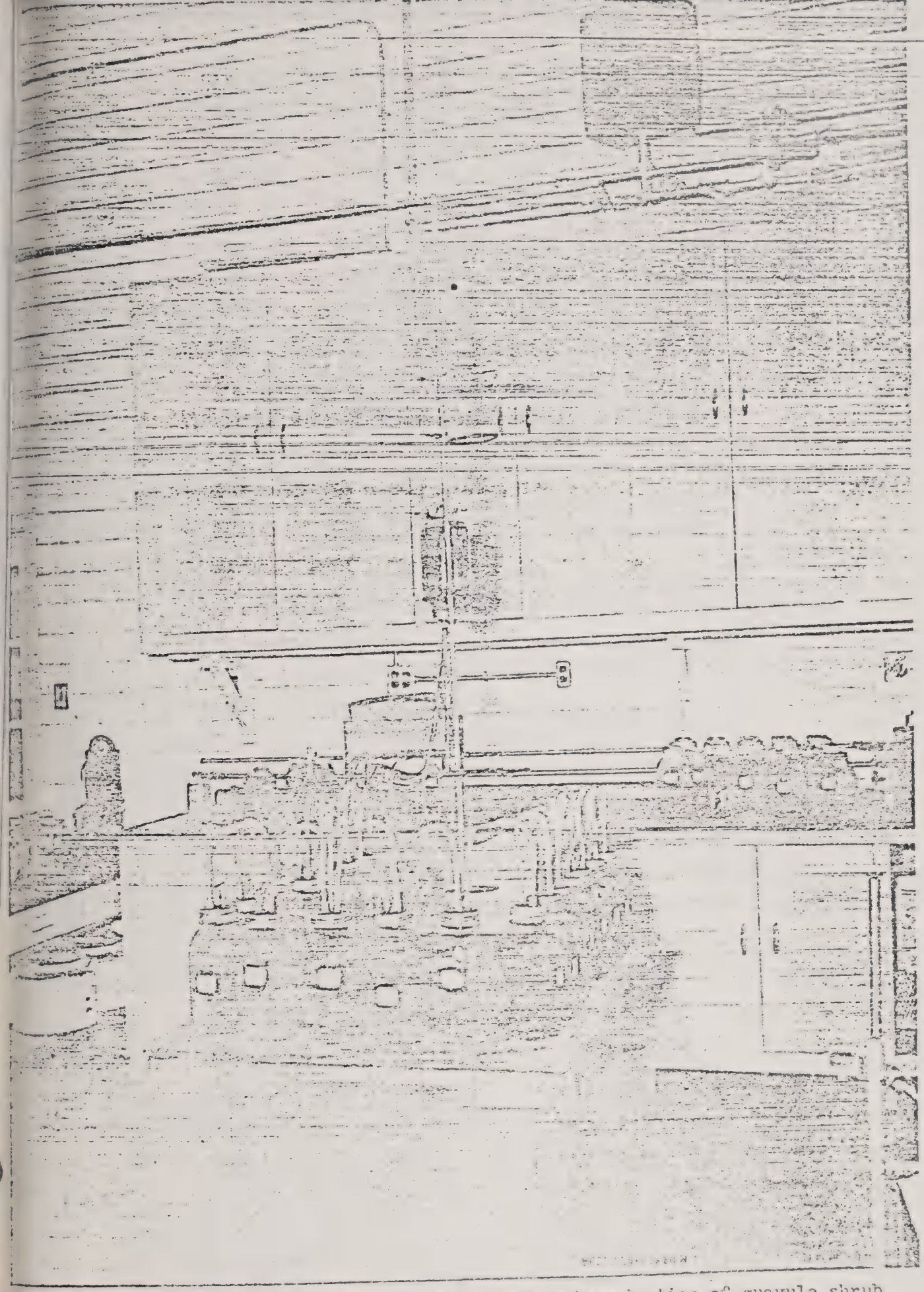
Comparison of baby jordan (center foreground) with tube mill. Both have approximately equivalent milling capacities.



General view of Pilot Plant

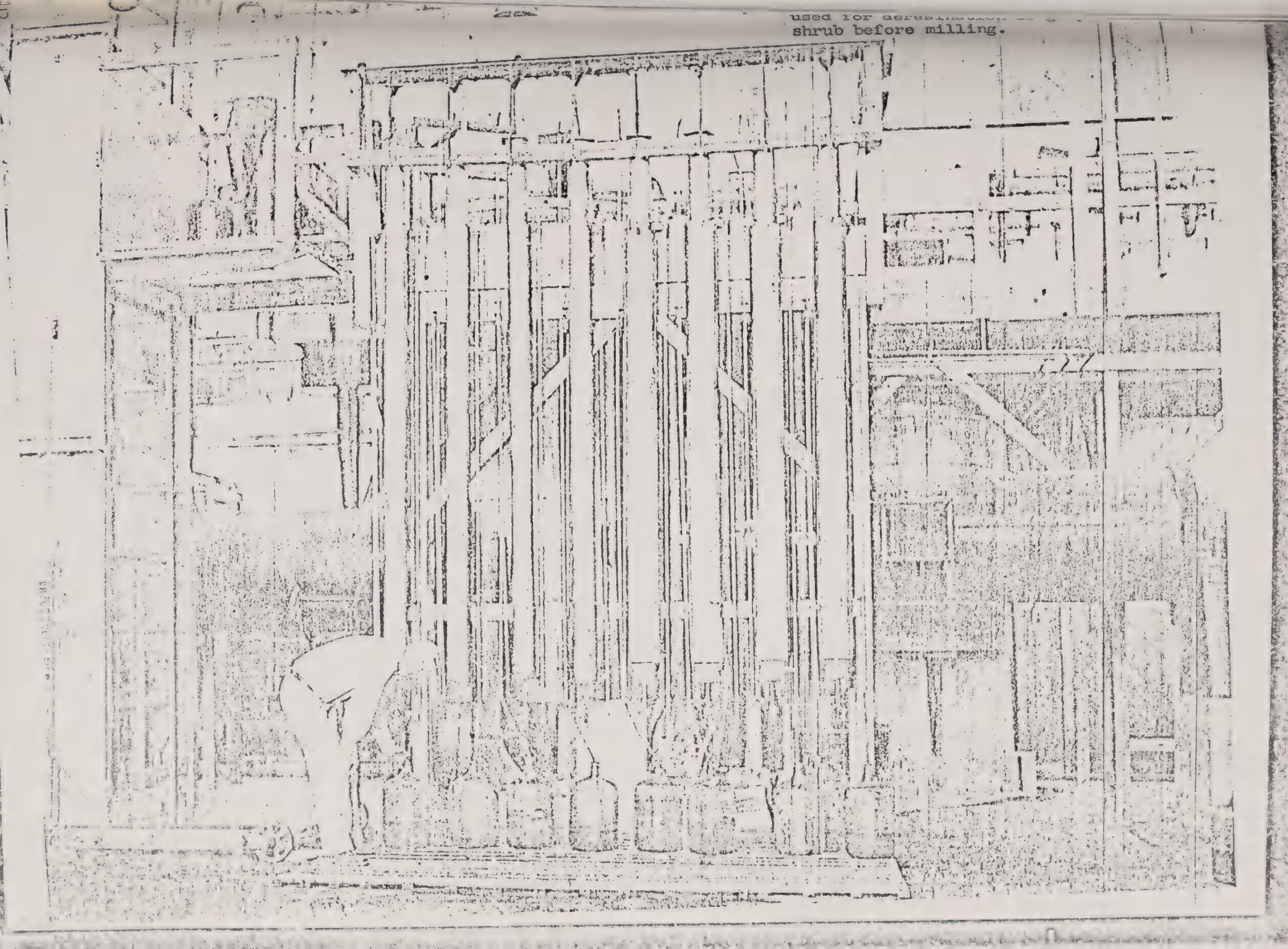


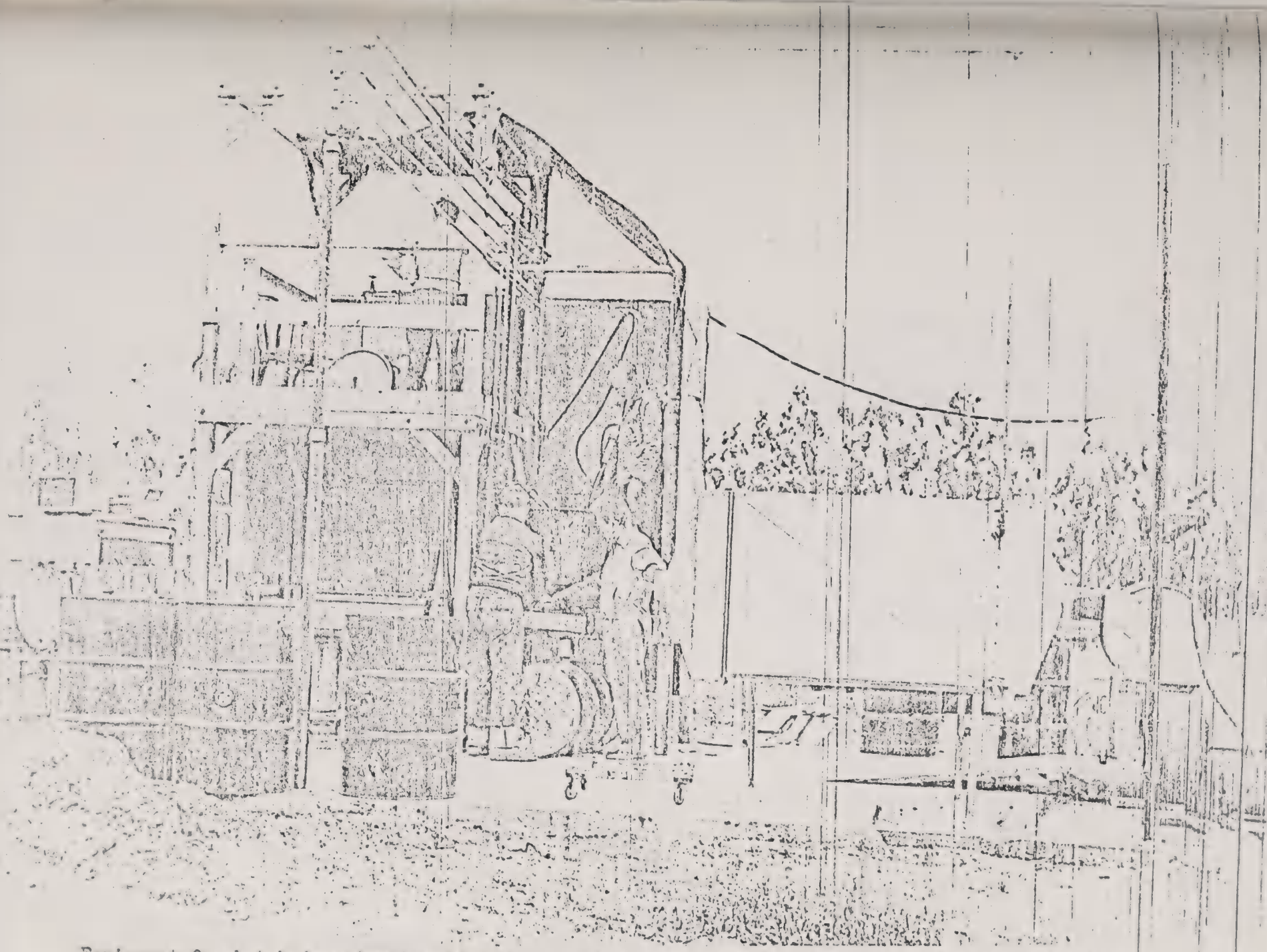
Continuous centrifuge for separation and concentration of guayule rubber latex



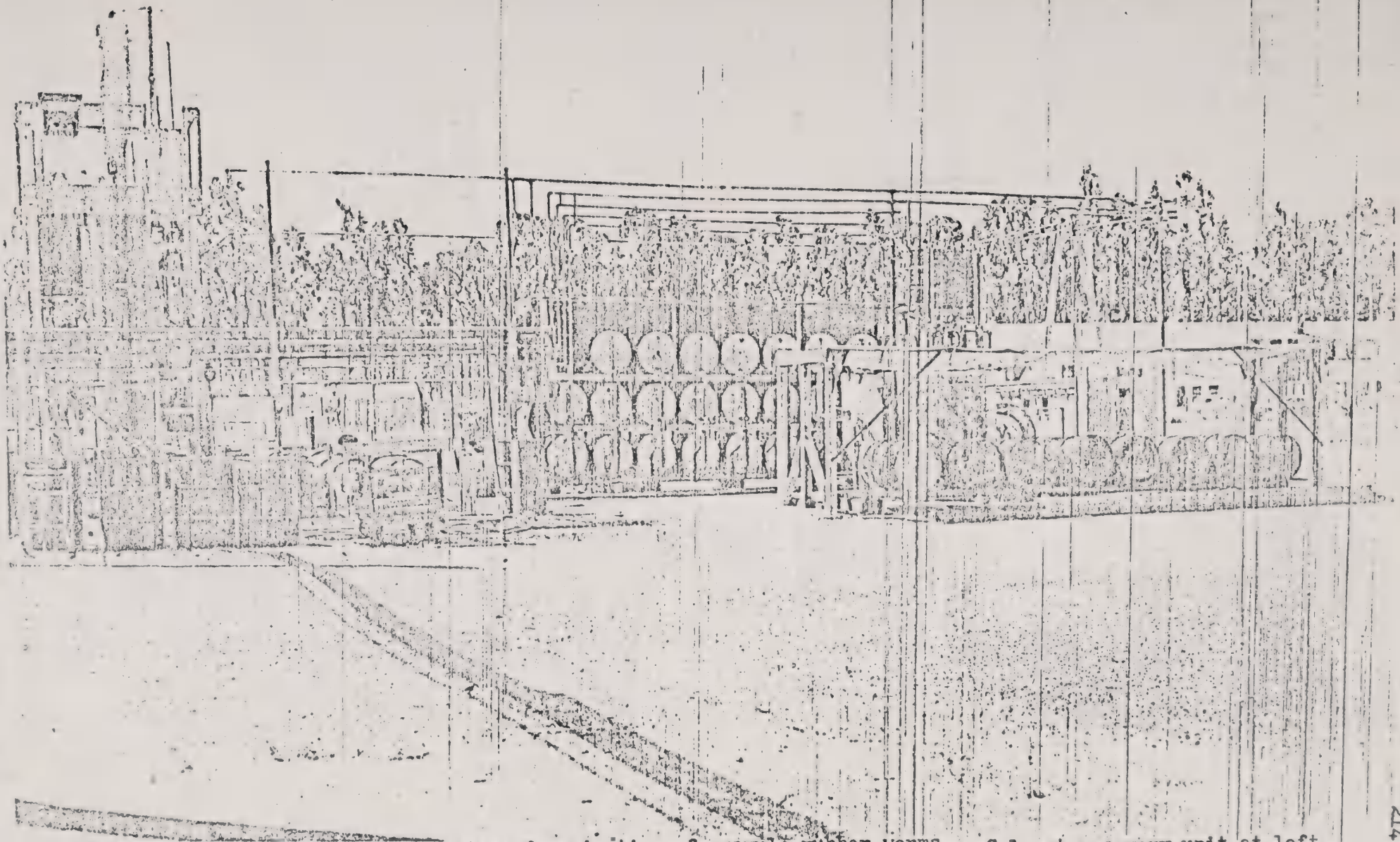
oratory countercurrent extraction system for acetone deresination of guayule shrub

used for deresination of
shrub before milling.

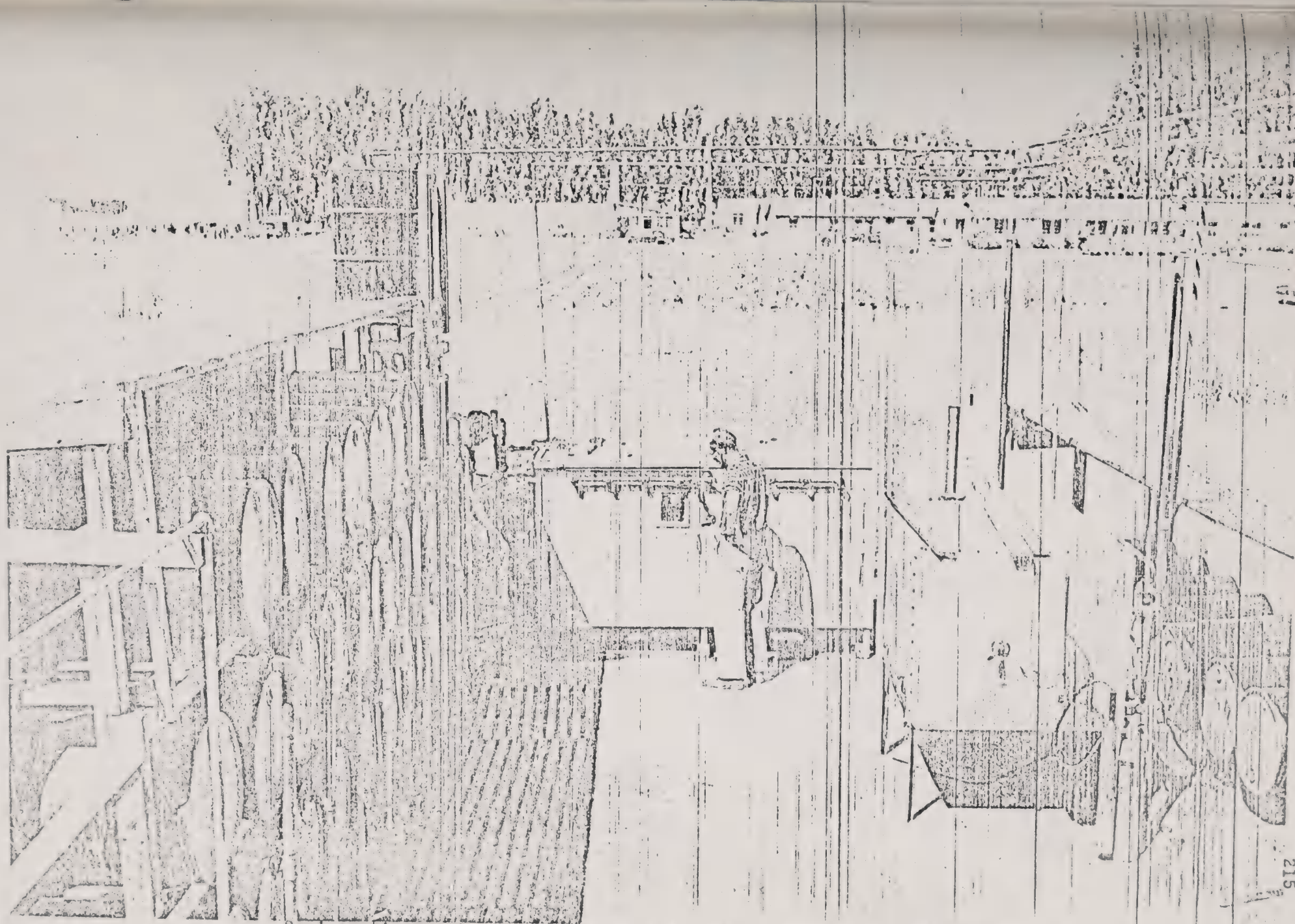




Equipment for batch deresination of guayule rubber worms used in early stage of process development

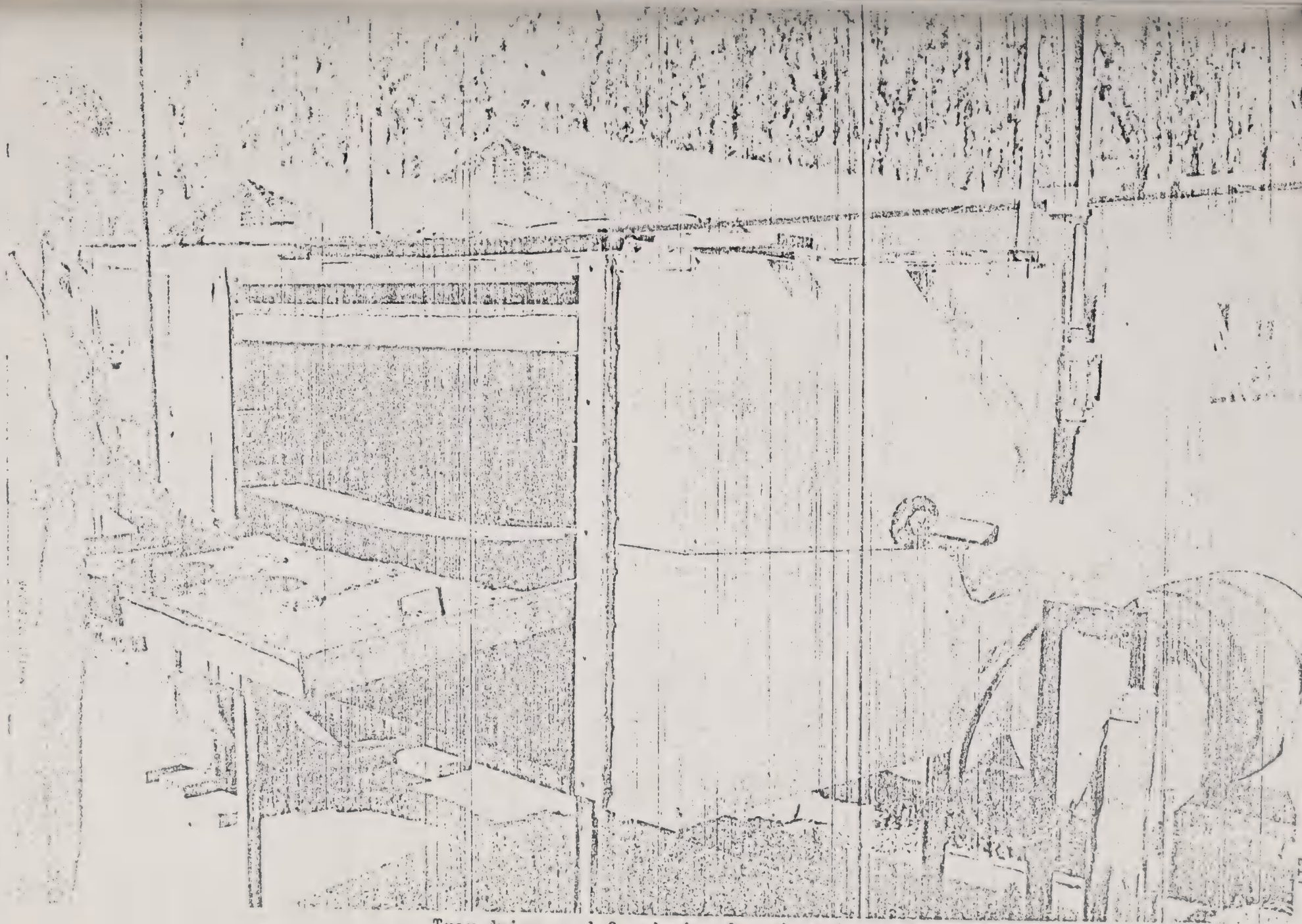


Installation for countercurrent acetone deresination of guayule rubber worms. Solvent recovery unit at left.

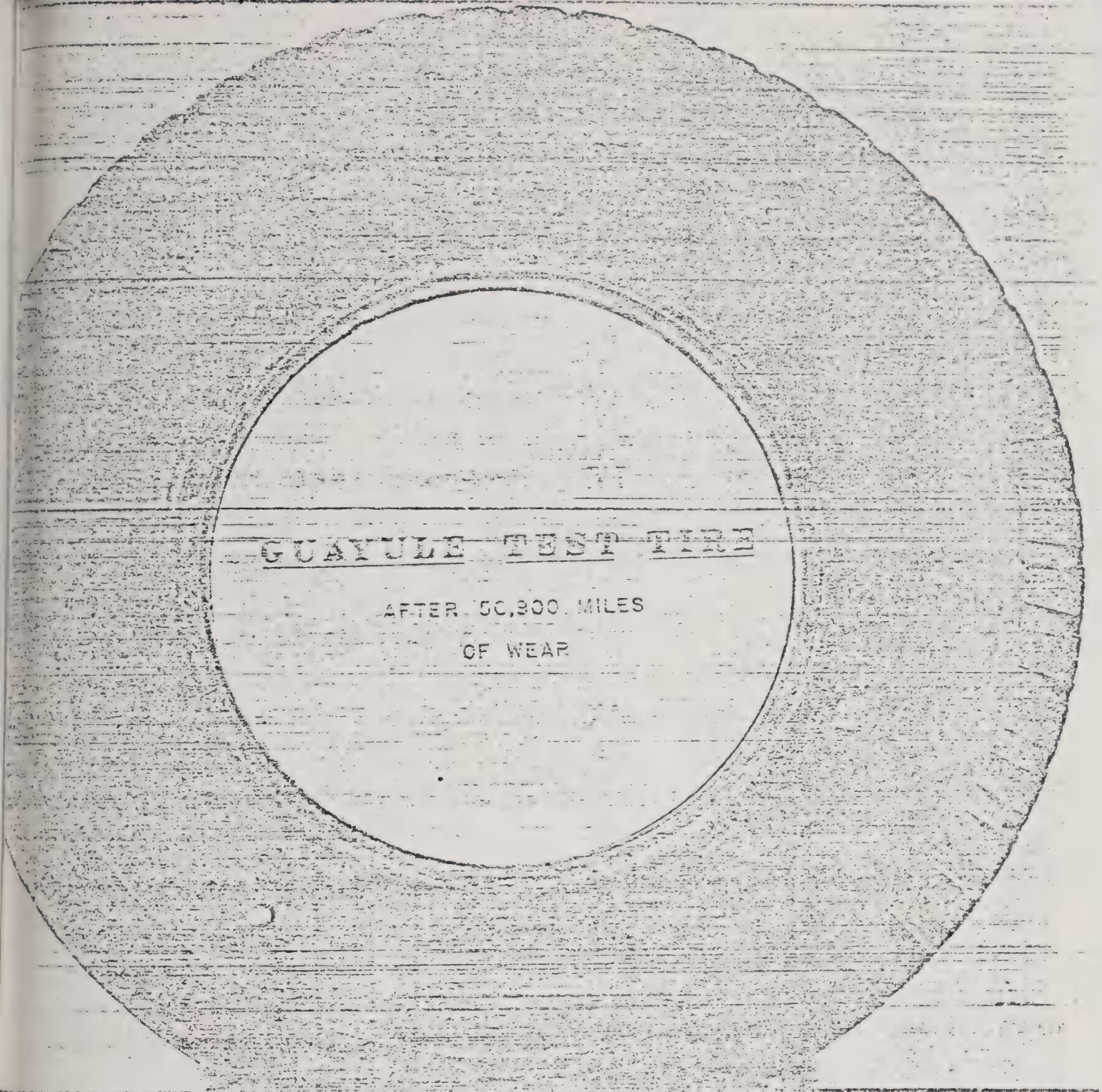


Semi-continuous installation for acetone deresination of resinous rubber worms

Sampling deresinated guayule rubber worms in tray deresinator



Tray drier used for drying deresinated guayule rubber

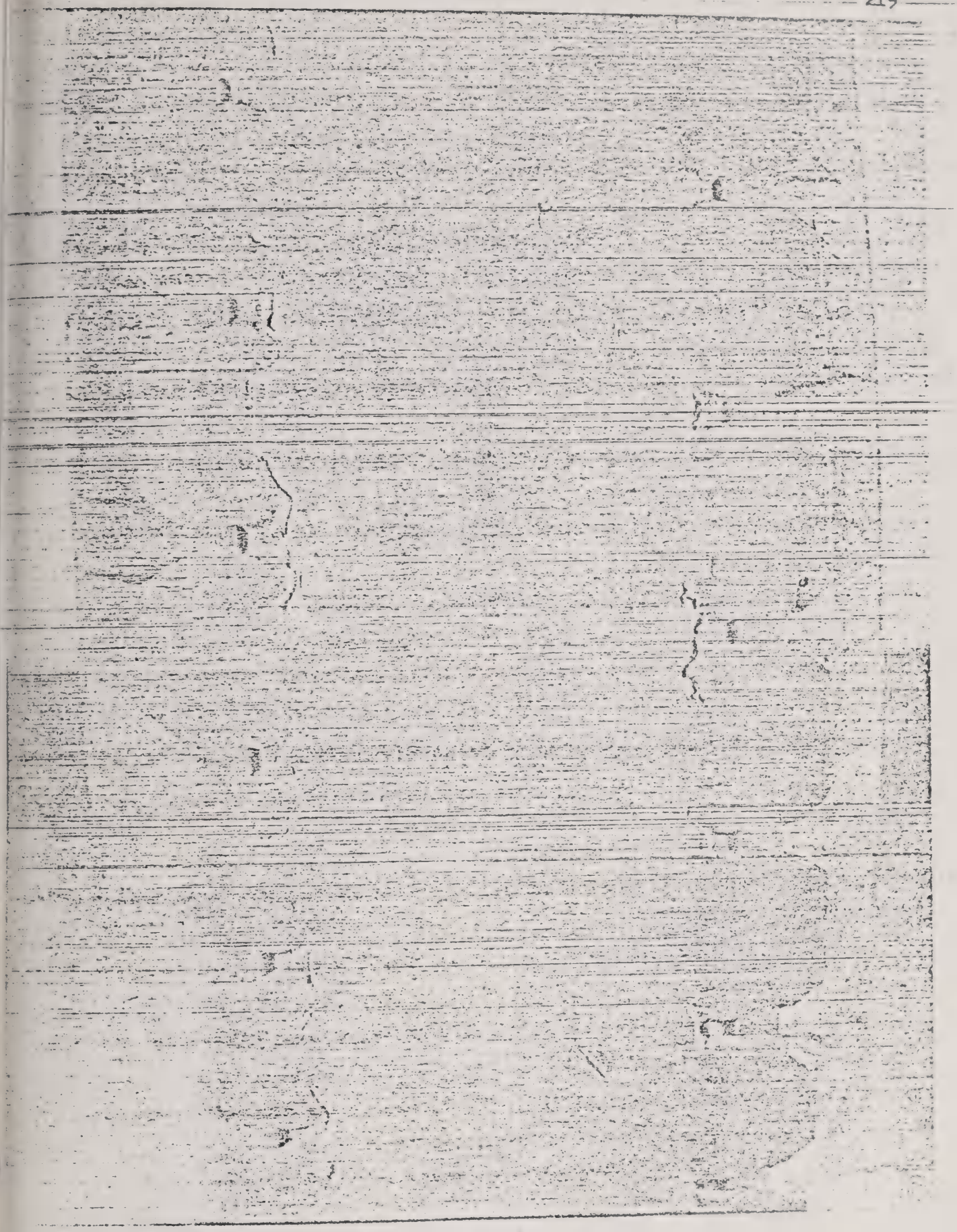


THIS - THE FIRST SUCCESSFUL TRUCK TIRE EVER BUILT OF GUAYULE RUBBER - WAS MADE POSSIBLE THROUGH [illegible] IN THE PIONEERING WORK AT THE U.S. NATURAL RUBBER RESEARCH STATION ON EAST ALISAL STREET, SALINAS

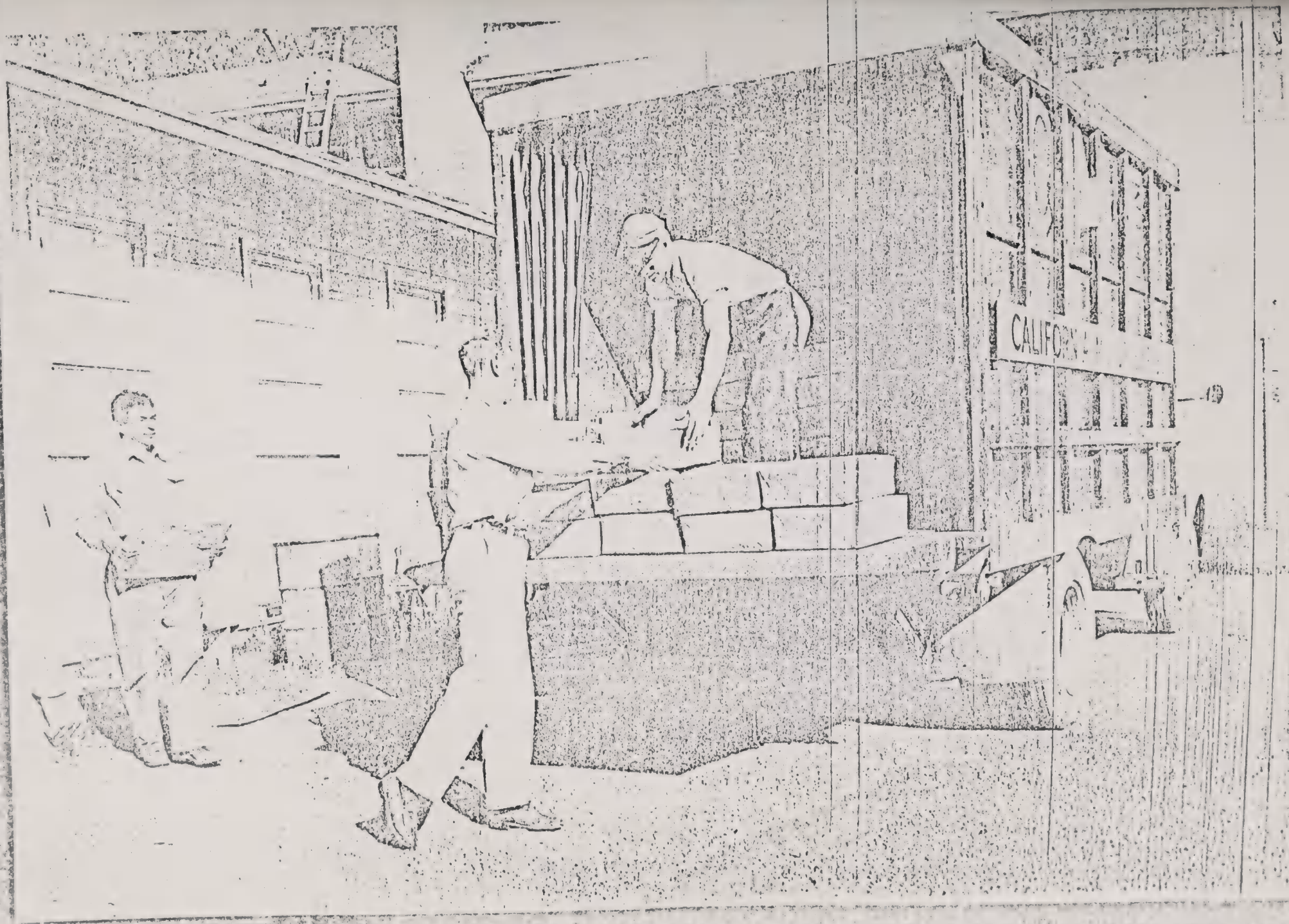
CARCASS CONSTRUCTION IS 100% GUAYULE NATURAL RUBBER WITH TREAD MADE OF SYNTHETIC 'COLD' RUBBER. ROAD TESTS, IN WHICH THE TIRE WAS RUN CONTINUOUSLY AT 45 MPH WITH APPROXIMATELY 40% OVERLOAD, WERE MADE BY THE OFFICE OF RUBBER RESERVE, CAMP BULLIS, TEXAS. GUAYULE PROVED TO BE THE EQUAL OF REGULAR PLANTATION RUBBER IN THESE TESTS.

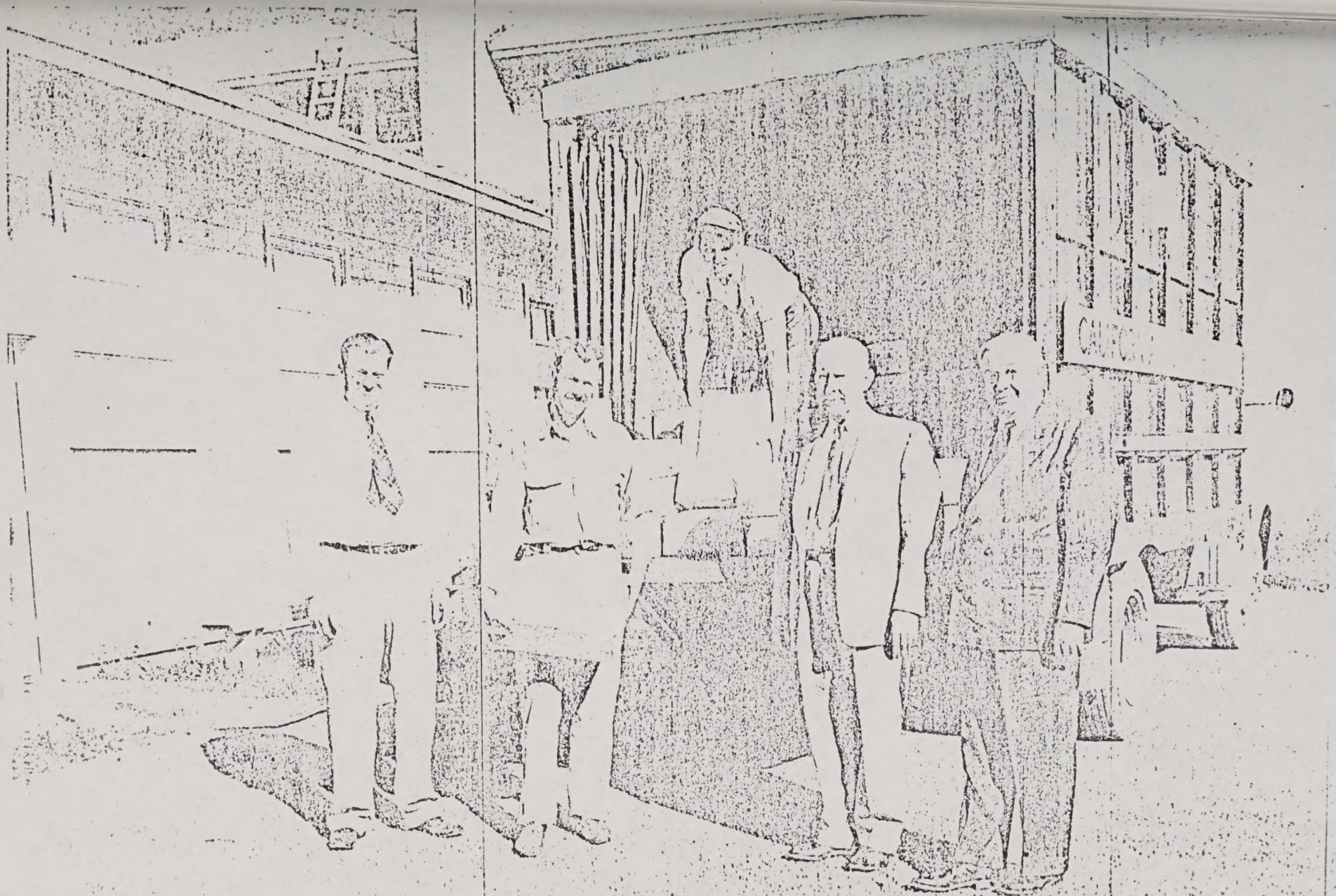
GUAYULE SHRUB FROM WHICH THE RUBBER WAS OBTAINED WAS GROWN IN THE SALINAS VALLEY BY THE BUREAU OF PLANT INDUSTRY, SOILS, & AGRICULTURAL ENGINEERING. THE RUBBER WAS EXTRACTED AND PURIFIED BY THE BUREAU OF AGRICULTURAL & INDUSTRIAL CHEMISTRY USING IMPROVED PROCESSING METHODS.

THIS TIRE, ONE OF A TEST LOT, WAS FABRICATED BY THE [illegible] TIRE & RUBBER COMPANY, AKRON, OHIO.



Tread of guayule test tire after 50,900 mile road test


CALIFO



Mr. C. F. Speh, Ass't Chief, BAIC and Dr. M. J. Copley, Director, Western Region, inspecting the last shipment of deresinated guayule rubber for industrial evaluation - 2500 lbs. for aircraft tire testing